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RENOVATION OF SEWAGE PLANT EFFLUENTS BY SOLVENT EXTRACTION

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Texas A and M Research Foundation
College Station, Texas

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RENOVATION OF SEWAGE PLANT EFFLUENTS BY SOLVENT EXTRACTION

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for

The Advanced Waste Treatment Research Program

Basic and Applied Sciences Branch

Robert A. Taft Sanitary Engineering Center

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ADVANCED WASTE TREATMENT

RESEARCH PROGRAM

The Advanced Waste Treatment Research Program of the Public Health Service has two ultimate goals: One is to help abate our Nation's growing water pollution problems, and the other, more startling in concept, is to renovate waste water for direct and deliberate re-use.

Conventional water and waste treatment practices have little or no effect on many simple inorganic salts and permit an ever-increasing number and amount of highly complex, synthetic organic wastes to contaminate drinking water supplies. If we are to protect these water supplies for the future, it is mandatory that new technologies for water and waste treatment be developed.

Advanced Waste Treatment may be looked upon as a two-step process: (1) Separating concentrated contaminants from the purified water "product," and (2) disposing of the concentrated contaminants in a way that will render them forever innocuous. This "permanent disposal" of separated wastes is essential so that useable surface or ground waters will not be contaminated and so that the same contaminants need not be removed again and again from water supplies.

In one step, then, advanced waste treatment, i.e., water renovation, could alleviate both water pollution and water supply

problems - - problems of increasing concern both in this country and in the rest of the world. The importance of advanced waste treatment was recognized by Congress in its 1961 amendments to the Federal Water Pollution Control Act (Public Law 87-88). This act directs the Secretary of Health, Education, and Welfare "... to develop and demonstrate practicable means of treating municipal sewage and other water-borne wastes to remove the maximum possible amounts of physical, chemical, and biological pollutants in order to restore and maintain the maximum amount of the Nation's water at a quality suitable for re-use."

It is too early to predict accurately the cost of advanced waste treatment technology, but the need is inevitable. Because of population increase and industrial expansion, we are approaching the time when our rivers and streams will no longer be able to assimilate our wastes and when there will be no more developable supplies of fresh water. Whatever the cost of this technology, one thing is certain -- <u>it must be the very lowest science and engineering can achieve</u>. Anything more will impose an inexcusable, perhaps intolerable burden on our country's growth and on its ability to compete in tomorrow's world.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of Mrs. Liverman and Mrs. Egli with the analytical work; Mr. Frank White for equilibrium studies on Na, Cl and Ca; and, Mr. Anton Vos in the building and operating of the continuous unit.

This report is the result of two years' work on the project. Some of the results of this investigation have been reported at the ACS meeting in Cincinnati, January 1963, at the ACS meeting in Philadelphia in April 1964 and at the AICHE meeting in Las Vegas in September 1964.

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RENOVATION OF SEWAGE PLANT EFFLUENTS

BY

SOLVENT-EXTRACTION

INTRODUCTION

A water quality renovation unit could solve both problems of water supply and water pollution simultaneously. All the methods used to reclaim salt water may also be used to partially purify secondary effluents. Some do not remove much of the organic matter, while many of the methods remove only inorganic constituents. Ion exchange, dialysis, and solvent extraction are especially adaptable to the low salinity prevailing in secondary effluents, but the first two do not remove, and may be adversely affected by the organic matter.

Solvent extraction offers the possibility of removing both organic and inorganic contaminants from sewage secondary effluents, and possibly at a cost lower than that for brackish water.

Background

The contaminants of challenge to advanced waste treatment processes are those resistant to, or even totally unaffected by today's best conventional water and waste treatment processes. Accordingly, these materials, termed "refractory" build up in water streams and can be the cause of serious economic and physiological damages.

Secondary effluents from sewage treatment plants usually contain only about 500 ppm dissolved solids, out of which 50 to 150 ppm is organic matter. The common inorganic ions are Na^{+}, Ca^{++}, Mg^{++}, Cl^{-}, SO_4^{--}, PO_4^{--}, and NO_3^{-} (1). Various efforts to analyze the organic contaminants have resulted only in pinpointing a few according to their exact structure. Some of these (2) have been found to be ABS, proteins, carbohydrates, tannins, lignins, long-chain hydrocarbons, and long-chain fatty acids.

The solvent extraction process operates on the principle that certain solvents which contain strong electronegative atoms within the molecule are partially miscible with water to an extent depending mainly on the temperature and the salt content of the water. Among 400 solvents that have been studied (3), 5 and 6 carbon atom, secondary and tertiary amines were found to have by far the best solvent properties. A schematic diagram of the process is shown in Figure 1. In essence the process consists of three basic parts, extraction, separation and solvent recovery. In Figure 2, the solubility curve of diisopropylamine (DIPA) is shown. In this curve the weight per cent of water in the solvent is plotted versus temperature for different salt concentrations. If one chooses an extraction temperature of 32°C, the solvent will dissolve approximately 30 per cent water from the one per cent salt solution. If the solvent represented is then heated to 55°C, all except

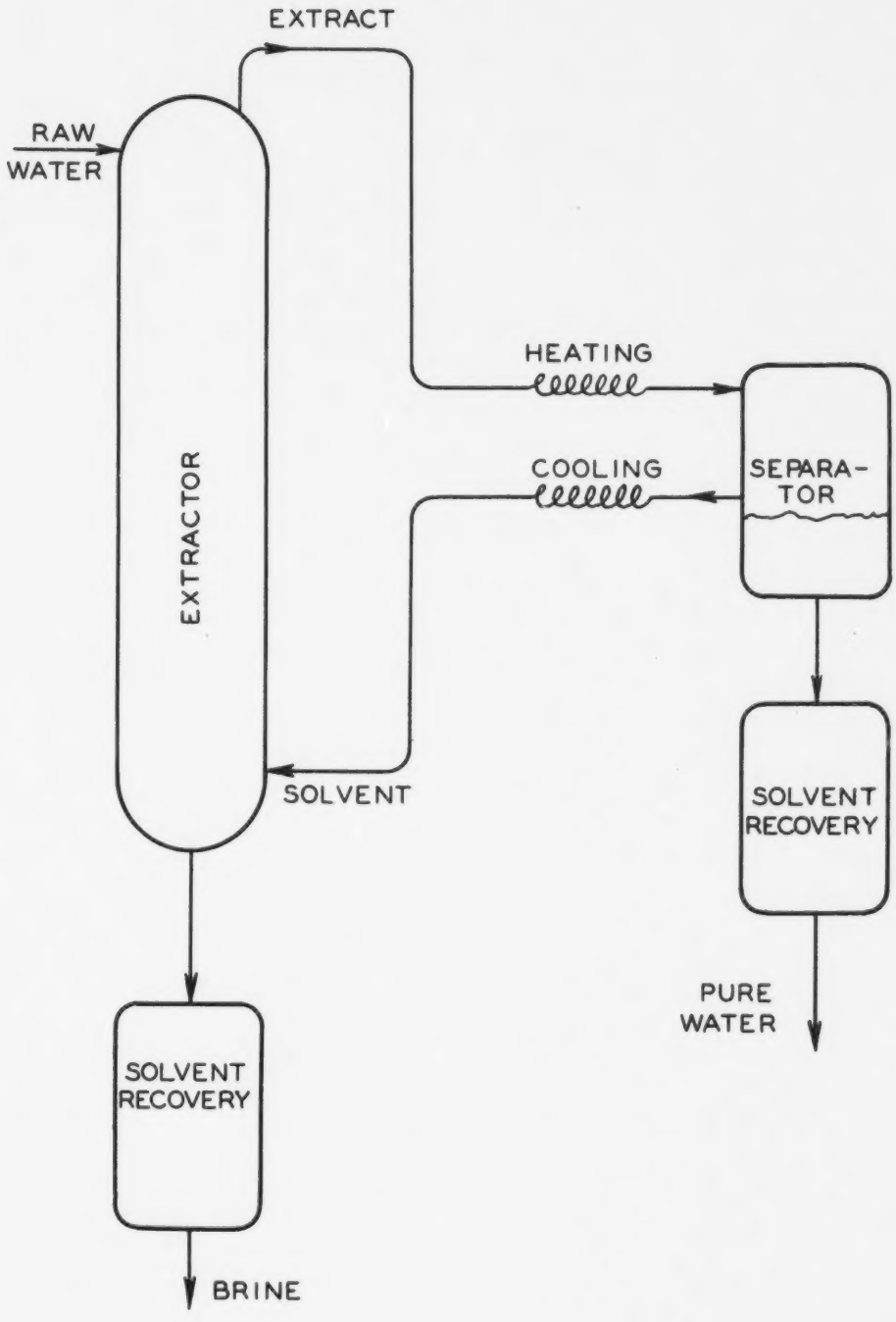
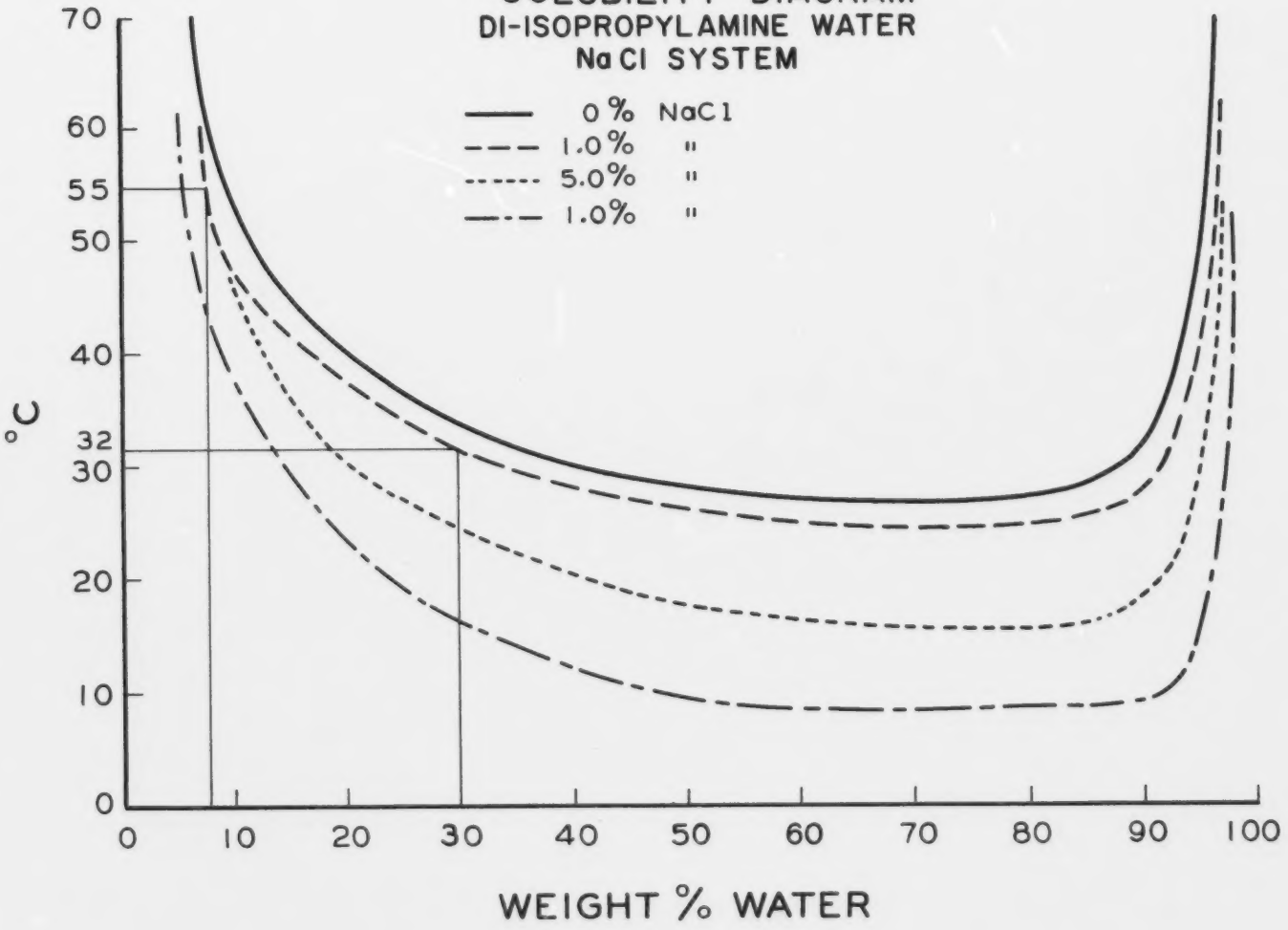


FIGURE I. SCHEMATIC DIAGRAM FOR SOLVENT EXTRACTION OF SALINE WATERS

FIGURE 2

SOLUBILITY DIAGRAM
DI-ISOPROPYLAMINE WATER
NaCl SYSTEM



eight per cent of the water phases out. After separation of the water and solvent phases, the solvent can be recycled to the extractor to make the process continuous. Full descriptions of the process as applied to saline water conversion can be found in the literature (3), (4), (5), (6).

One of the main differences between waste treatment and saline water conversion is that the types of impurities of challenge in water-born wastes are very different from those in saline waters. Mainly the organic contaminants in waste waters are of more concern than those in most saline waters. The waste water renovation problem is dynamic whereas the saline water problem is static. In other words, in a waste treatment plant, the process must be ready to accommodate a feed stream that is changing in composition and concentration continuously.

RESEARCH OBJECTIVES AND PLAN OF INVESTIGATIONS

The evaluation of the solvent extraction process for the reclamation of sewage secondary effluent was the main objective of the investigation carried out during the two-year period ending July 1, 1964. The first year was spent on the modification of the analytical methods to accommodate the solvent system and to study the distribution of both organic and inorganic contaminants between the solvent extraction streams. This was carried out for single stage batch extraction and

the evaluation of tritium labeling of organic matter in the sewage samples as a method to study organic matter distribution were also carried out.

During the second year of the contract two main areas were investigated. First, the distribution of different cations and anions found were studied using standard solutions of each. The object was to determine the equilibrium constants for the distribution of these ions in the solvent-water system.

The organic matter distribution in the solvent extraction streams was studied using samples of secondary effluents from local sewage treatment plants. Second, the study of coagulation pretreatment prior to solvent extraction to remove the organic matter that contaminates the solvent was carried out. The continuous extraction unit was rebuilt to include a reflux column. The distribution of inorganic and organic contaminants using reflux was studied to find out the limiting operation conditions that results in the best quality of product.

SAMPLING AND ANALYTICAL PROCEDURES

The first phase of this study was the selection of reliable analytical methods to accommodate the solvent system. It was also necessary to study the natural changes occurring in the waste samples and to find a means of preserving a sample over a period of time sufficient for testing.

Sampling

All the local sewage treatment plants in the Bryan-College Station Area are combined sewerage units that consist of primary settling, trickling filters and secondary settling. The Bryan Plant serving the City of Bryan, has the highest capacity of all local plants and receives wastes from some industries and coin operated laundries. This plant effluent was used primarily in these studies. Samples were collected, during the morning peak hour, in five gallon polyethylene jugs from the overflow of the secondary settling tank. The sample, filtered through a Whatman No. 5 filter paper, was then heated to 180°F (82°C), then held at that temperature for ten minutes, and cooled to room temperature before storage at 4°C. This treatment was carried out on the first day after a sample was collected and the analyses were made over a fourteen day maximum storage period. COD analyses of a filtered sample which were stored at room temperature and of a pasteurized sample stored at 4°C, were compared over a period of fourteen days (Figure 3). The change in COD value of the pasteurized sample was less than ten per cent over the two week period. Analyses for chloride, T.S., V.S., and ABS did not change during the storage period. Samples collected for the batch extractions and equilibrium studies were preserved by the pasteurization treatment, and the COD was determined on each sample every other day as a check.

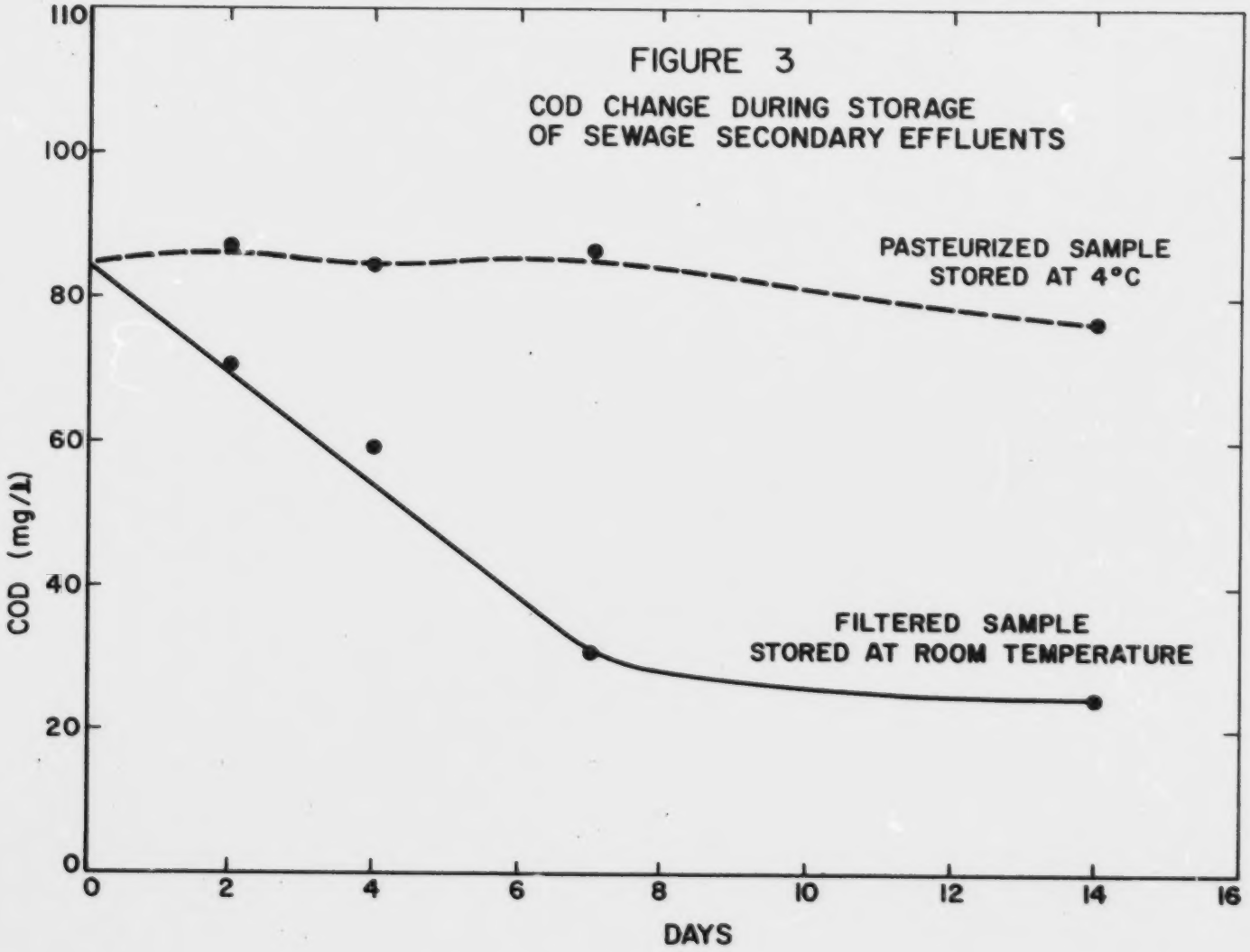


FIGURE 3
COD CHANGE DURING STORAGE
OF SEWAGE SECONDARY EFFLUENTS
PASTEURIZED SAMPLE
STORED AT 4°C
FILTERED SAMPLE
STORED AT ROOM TEMPERATURE
COD (mg/L)
DAYS
0
20
40
60
80
100
110
0
2
4
6
8
10
12
14
16

The range and average analyses of secondary effluents collected from Bryan Sewage Plant are given in Table I. These values compare very well with the eastern average of the United States.

Analytical Procedures

Standard analytical methods (7), modified to accommodate the solvent system, were used for the routine analysis of the solvent extraction streams. The diisopropylamine used throughout this study is soluble in water and will interfere in the analysis of COD, ABS, NO_3^-, and conductivity. Since the correction for DIPA in COD determination is very high (1 mg DIPA equivalent to 2.85 mg COD), methods were devised to eliminate the amine interference by stripping with air or distillation prior to running the analysis. The results of the studies are indicated below.

Chemical Oxygen Demand (COD). The dichromate reflux method as described in the Standard Methods for the Examination of Water and Waste Water (7) was followed during the early stages of this investigation. A reflux period of 45 minutes, followed by the addition of the catalyst, silver sulfate, then refluxing for 75 minutes, gave reproducible results when the chloride correction was applied. Later, a modification of the procedure (8) using mercuric sulfate to eliminate the chloride interference was checked against the standard procedure and found to be reliable. This method was followed through the later part of this investigation.

Air stripping of amine-water solutions for 1.5 hours at 60°C

Table 1

Average Analysis of Secondary Effluent

Bryan Sewage Plant

Analysis	Range	Average[a]	Eastern Average[b]
Chloride mg/l	45.8 - 69.5	59.5	83
COD mg/l	85 - 120.7	98.7	97
ABS ppm	3.7 - 6.7	4.85	5
T.S. mg/l	417 - 595	485	497
V.S. mg/l	128-200	158	-
Nitrate mg/l	9.5 - 43	-	13
Phosphate mg/l	18.8 - 28.8	-	25
Sp. conductance µmhos/cm	632 - 900	768	-

(a) Average of 7 samples collected over a period of 4 months during the morning peak hour.

(b) Values from Average Secondary Effluent circulated by Advanced Waste Treatment Research Program, U.S.P.H.S.

results in high residual COD values. This is believed to be due to the CO_2 in the air. Distillation of aqueous solutions removed the bulk of the amine. The DIPA was distilled off as an azeotrope at 74°C. The pH of the solution was then raised from 8 to 11 by the addition of a few drops of NaOH solution, and the solution was redistilled at 100°C for five to ten minutes. This treatment was found to remove the last traces of the amine and eliminate any interference in the COD analysis.

Samples of the filtered sewage effluents when boiled for one hour and the original volume made up with distilled water, were found to exhibit a reduction in COD of less than five per cent.

During the extraction tests a blank was used as a control and the distillation procedure was used to eliminate the amine from both the product and raffinate prior to analysis for COD.

Alkyl Benzene Sulfonate (ABS). The modified Methylene Blue method for use by Advanced Waste Treatment Research Contractors was followed. The DIPA was found to compete with methylene blue in the ABS analysis resulting in a 20% reduction of the ABS concentrations. It is believed that DIPA forms a complex with ABS that is partially broken by methylene blue. The distillation treatment of samples, as explained under COD analysis, was found to remove the amine completely, resulting in no interference in the ABS analysis.

Chloride. The chloride ion was determined by two methods;

a) Mohr Method [7]: Titration of the chloride with standard silver nitrate in presence of potassium chromate indicator.

b) Amperometric Titration Method[9]: The chloride ion concentration was determined by titration against standard $AgNO_3$ solution, 0.01N. The end point is detected by silver-silver chloride electrodes connected to a bridge-type vacuum tube voltameter circuit.

In both methods, the amine does not interfere and samples were analyzed either before or after the distillation treatment.

Specific Conductance. The electrical resistance of solutions was measured using a platinized platinum electrode connected to an impedence bridge and a cathode ray oscillcgraph. Samples and standard potassium chloride solution 0.01 N were placed in a water bath at a constant temperature near room temperature. The specific conductance of the sample at 25°C was then calculated from the following equation:

$$\text{Specific Conductance} = \frac{1411.8 \times R_{KCl}}{R \text{ sample}} \mu \text{ mhos/cm.}$$

The specific conductances of raffinates and products were measured after the removal of the bulk of the amine by distillation, but before the addition of any NaOH to the sample.

Total Solids (T.S.) and Volatile Solids (V.S.). The total dissolved solids in filtered secondary effluents was determined following the standard methods [7]. The loss by ignition at 600°C for 10 minutes was recorded as volatile solids. The volume of samples used for this determination was 50 or 100 ml.

Nitrate. The brucine colorimetric method [10] for nitrate ion in industrial water was used. Samples were distilled free of amine before this analysis because of the vigorous reaction of the amine with concentrated H_2SO_4.

Phosphates. The phosphate ion in sewage samples, raffinates and products was determined with the colorimetric, Amino-Napthol-Sulphuric Acid method [7].

BATCH EXTRACTIONS

The objects of the preliminary investigations were to study the behavior of ABS, in particular, and other contaminants as measured by T.S. and COD tests, when secondary sewage effluents were extracted with DIPA. A procedure of extraction and conditions most favorable for removal of contaminants had, then, to be devised.

Apparatus. A basket was built to hold four 1-liter separatory funnels. The basket fits in the rotating mechanism inside a water bath the temperature of which was controlled to $\pm$ 0.1°C. A spring was fitted to the stopper of each separatory funnel to hold it tight during

the mixing period.

Procedure. Measured weights of water samples and amine solvent were well mixed in the separatory funnels and placed in the water-bath regulated at the extraction temperature. Then mixing by rotation was continued for 1 1/2 hours to obtain equilibrium between phases. At the end of the mixing period, the phases were settled for 15 minutes, then separated. The raffinate phase was weighed, filtered when necessary, and then distilled to remove the amine. The extract left in the separatory funnels was placed in the water bath, without mixing, for one hour, at the separating temperature. The product was then separated, weighed and distilled to remove the amine. The solvent phase was weighed and distilled to recover the amine for reuse. The residue, made alkaline to pH 12 was then re-distilled to remove the last traces of the amine and diluted to 250 ml with distilled water. The raffinate, product and solvent residue were then analyzed by the above methods.

Preliminary Tests. The results of ABS extraction from standard solutions and waste effluents are given in Appendix I[illegible].

Several extraction experiments were made on sewage samples 2 and 3, analyzing the streams for Cl^-, COD and ABS. Different ratios of $\frac{DIPA}{Feed}$ were used at extraction temperatures of 32°C to 35°C. The separation temperature was 50°C. The higher extraction temperatures resulted in less water extracted, thus less product. Results of these preliminary tests are summarized in Table 2.

Table 2

DIPA-Extraction of Sewage Samples No. 2 & 3

Preliminary Tests

Sewage Sample No.	DIPA Feed Ratio	Extraction Temperature °C	Feed Analysis mg/l			Raffinate Analysis mg/l			Product Analysis mg/l		
			COD	Cl^-	ABS	COD	Cl^-	ABS	COD	Cl^-	ABS
2	4/3	32	85	61.4	10.9[1]	195	88	0.20	20.6	42.5	0.48
2	4/3	32	85	61.4	17.6[1]	168	88	0.24	21.0	42.5	0.44
3	4/3	35	85.5	45.8	4.5	135	53.2	0.40	23.6	17.5	0.52
3	2/1	35	85.5	45.8	4.5	177	65.9	0.48	28.0	24.2	0.56
3	8/3	35	85.5	45.8	4.5	194	102	0.36	10.8	38.1	0.60
3	2/1[4]	35	76[3]	45.8	4.5	52.9	70.6	0.24	29.1	22.0	0.40
3	2/1[5]	35	62.7[3]	45.8	4.5	280.0	128.9	0.15	42.0	31.1	0.24

[1] ABS standard solution added to sewage sample

[2] Sewage sample 7 days old, COD dropped from an initial value of 85.5

[3] Sewage sample 13 days old, COD dropped from an initial value of 85.5

[4] Redistilled DIPA

[5] Pure DIPA

The selectivity of extraction of the organic matter, as measured by COD analysis, seemed to be as good as the chloride ion selectivity. The ABS was removed by the solvent and its concentration in both the raffinate and the product was lower then 0.6 ppm. An extraction temperature between 32° and 35°C was found to yield a product of good quality. A ratio of solvent to water sample of 2:1 was chosen since it was the most convenient to use in the available apparatus.

Batch Extraction of Sewage Samples No. 4 and 5. The analyses of sewage samples No. 4 and 5 are given in Appendix 1. Batches of filtered samples were mixed with redistilled DIPA in the ratio 1:2, by weight. An extraction temperature of 35°C and a separation temperature of 50°C were used. The raffinates and products were filtered, the amine removed by distillation, then analyzed for COD, Cl^-, ABS, T.S., V.S. and conductivity.

The analytical results and materia' balances are given in Tables 3 and 4. Figures 4 and 5 show the distribution of Cl^-, COD, ABS, T.S. and V.S. for both extractions. The dotted lines show the calculated values of T.S. rather then the analytical values.

The selectivity of extraction of organic contaminants, as measured by COD, and V.S., and inorganic contaminants, as measured by Cl^- and T.S. is defined as the concentration of a component in the raffinate phase divided by its concentration in the product phase.

FIGURE 4

BATCH EXTRACTION OF SEWAGE SAMPLE NUMBER 4

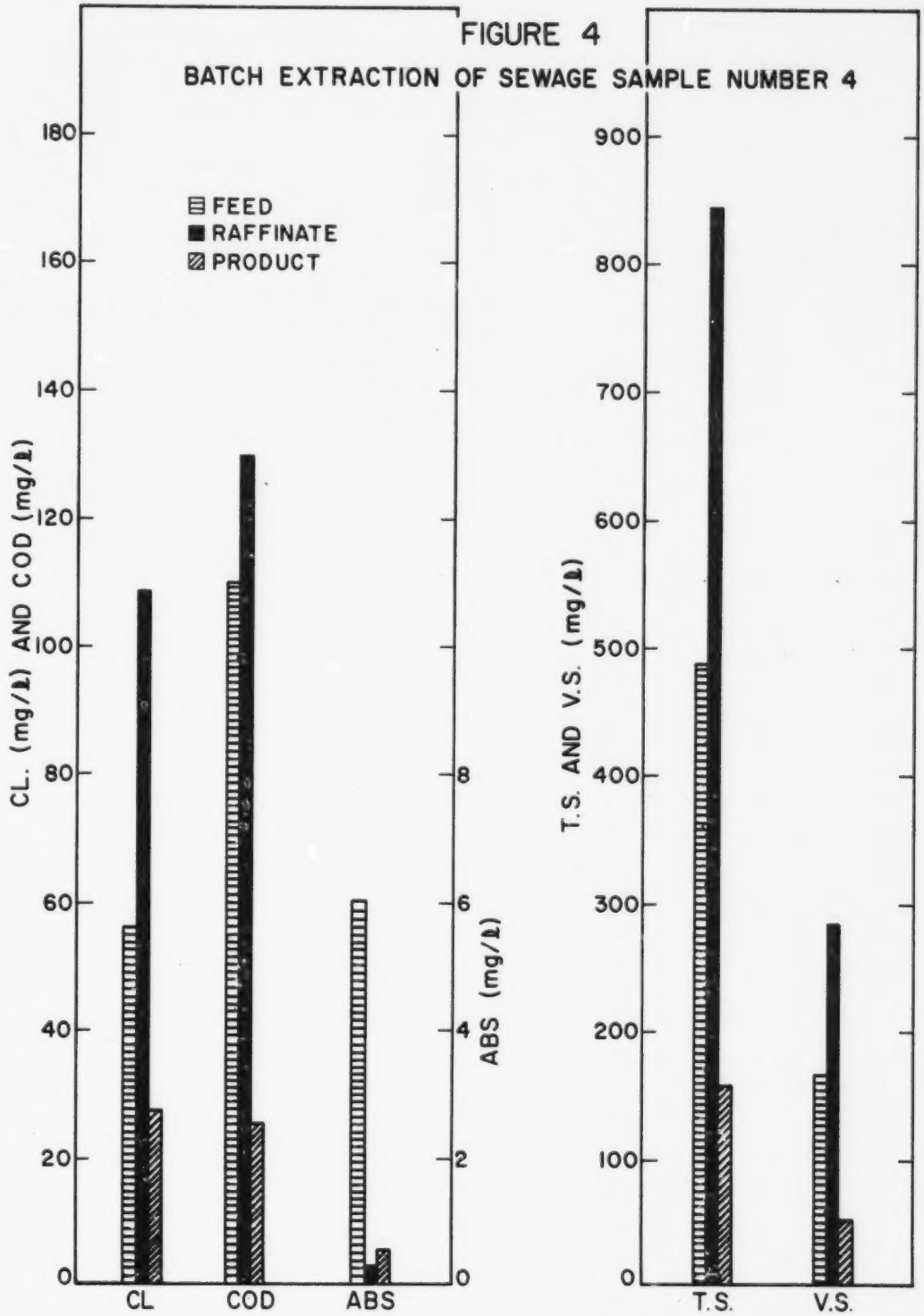


FIGURE 5

BATCH EXTRACTION OF SEWAGE SAMPLE NUMBER 5

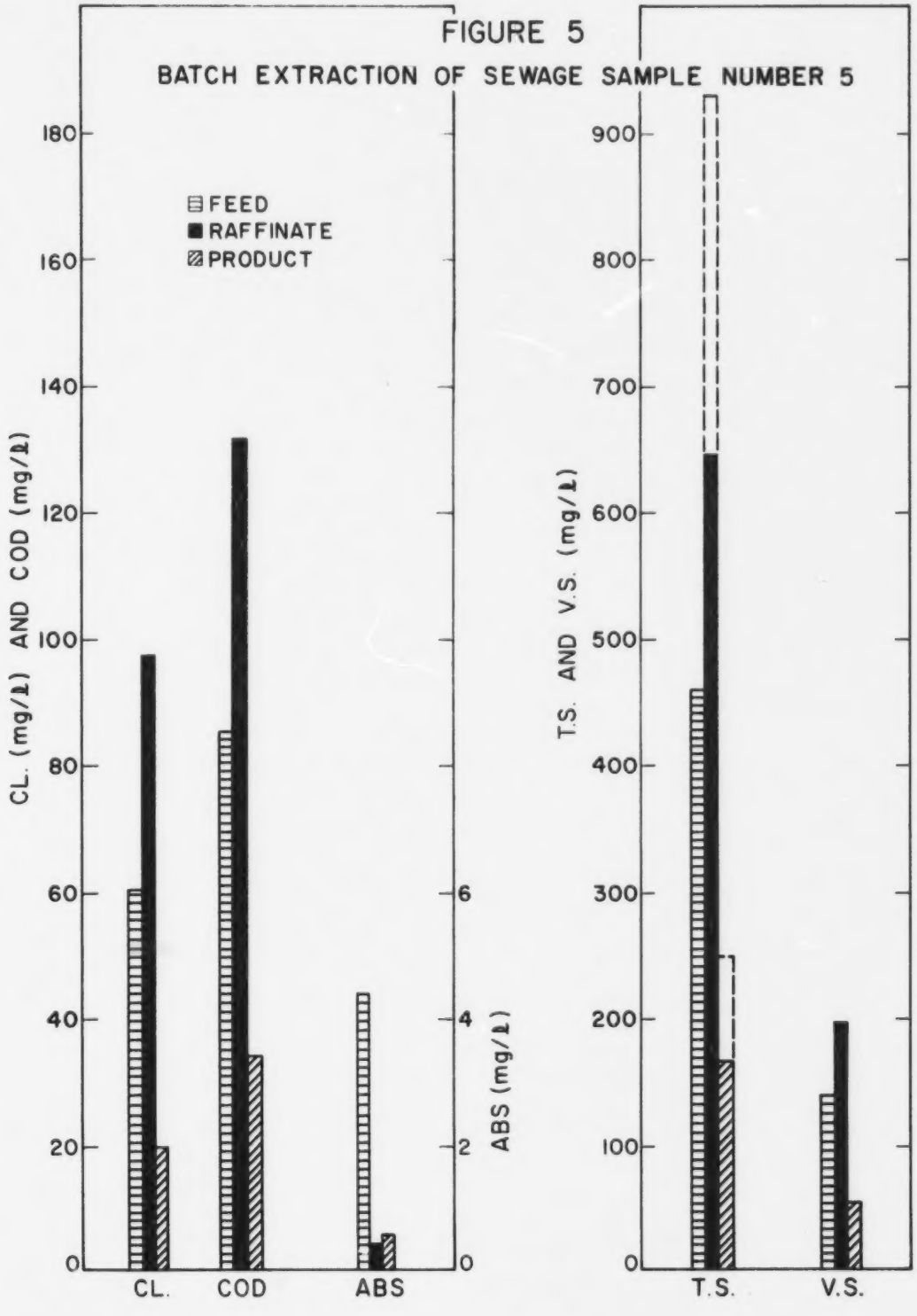


Table 3

Extraction of Sewage Sample No. 4

Feed ---------- 800 ml

Redistilled DIFA------- 1600 gm

Raffinate = 348 gm[1]

Product = 318 gm[1]

Solvent = 1570 gm

	Chloride		COD		ABS		Sp. cond.	T.S.	V.S.	T.S calculated[2]		V.S. calculated[2]	
	mg/l	mg	mg/l	mg	mg/l	mg	µmhos/cm	mg/l	mg/l	mg/l	mg	mg/l	mg
Feed	56.15	44.92	110.5	88.4	6.0	4.8	780	486.5	162.5	486.5	389.2	162.5	130
Raffinate	108.9	37.80	130.5	44.4	0.26	0.09	1353	-----	209	844.3	295.5	282.8	98.4
Product	26.9	8.64	25.4	8.1	0.50	0.16	252.6	141	75	157.6	50.4	52.8	16.8
Solvent	0.0	0.0	-----	38.2	----	4.75	-----	-----	-----	-----	43.3[3]	-----	14.8[2]
TOTAL		46.44		90.7		5.00					389.2		130

(1) Weights free of solvent.

(2) T.S. and V.S. as calculated from specific conductance values and the ratios $\frac{\text{T.S.}}{\text{specific conductance}} = 0.624$ and $\sqrt{\frac{\text{T.S}}{\text{specific conductance}}} = 0.415$ of the sewage water sample.

(3) These values are calculated by difference.

Table 4

Extraction of Sewage Sample No. 5

Feed---------- 1600 ml Raffinate = 848 gm[1]

Redistilled DIPA-- 3200 gm Product = 622 gm[1]

Solvent = 3200 gm

	Chloride		COD		ABS		sp cond.	T.S.	V.S.	T.S. calculated		V.S. calculated	
	mg/l	mg	mg/l	mg	mg/l	mg	µmhos/cm	mg/l	mg/l	mg/l	mg	mg/l	mg
Feed	60.4	96.64	87.7	146.3	4.4	7.04	742.7	462	140	-----	739.2		224
Raffinate	97.8	82.93	132	111.94	0.46	0.39	1037.7	930	350	645.6	547.5	196.3	166.4
Product	20.0	12.44	34.6	21.52	0.60	0.37	271.7	250	108	169.0	105.1	52.5	32.7
Solvent	0.0	0.00	25	80.0	----	9.00	-----	---	---	-----	86.6[2]	----	24.9[2]
TOTAL		95.37		213.46		9.76					739.2		224

(1) Weights free of solvent.

(2) These values are calculated by difference.

Table 5 gives these selectivities as obtained in batch extractions of sewage samples 4 and 5. The per cent distribution, as calculated from material balances, for COD, ABS, Cl^- and T.S. is given in Table 6.

Most of the total dissolved solids were concentrated in the raffinate; about 75% of those in the feed. The 11% of the T.S. that remained in the solvent phase should be mostly organic in nature. Over 80% of the chloride ion was concentrated in the raffinate with a selectivity factor of over 4.0. No chloride ion was detected in the solvent phase that still contained 10-12% water after product separation. The specific conductance of the raffinate was 3.8 to 5.4 times higher than that of the product, which indicates a good selectivity of ionizable materials, mostly inorganic in nature.

About 50% of the COD was concentrated in the raffinate and 40% in the solvent phase. Only 9 to 10% of total COD in the feed went into the product.

At this point of the investigation, it was clear that a product of good quality could be obtained in a one stage extraction, but a large percentage of the organic contaminants, including ABS, accumulated in the solvent phase. The solvent re-use had then to be tested.

Consecutive Extractions of Sewage Sample No. 6 with DIPA (Solvent Re-use)

The analysis of sewage sample No. 6 is given in Appendix II. A volume of 800 ml of this sample was extracted with 1600 gm of pure DIPA. About 200 gm of the solvent from extraction one were used for

Table 5

Selectivity of Extraction of COD, Cl^-, T.S. and V.S.

Component	Ratio of $\frac{\text{Concentration in raffinate}}{\text{Concentration in product}}$	
	Extraction of Sewage Sample 4	Extraction of Sewage Sample 5
COD	5.1	4.0
Cl^-	4.0	4.8
T.S.	5.4	4.0
V.S.	3.0	3.5

Table 6

Distribution of Organic Matter, ABS, Cl^-, and T.S. in Solvent Water System

Stream	% COD		% ABS		% Cl		% T.S.	
	Sample No. 4	5	4	5	4	5	4	5
Raffinate	49	52.6	1.8	4	81.4	87	75.9	74.2
Product	9	10.1	3.2	3.8	18.6	13	12.9	14.3
Solvent	42	37.3	95.0	92.2	00.0	0.0	11.2	11.5

analysis and the remainder was used to extract 1/2 its weight of sewage sample. The same procedure was repeated for five consecutive extractions. The extraction temperature was always 35°C and the product was separated at 50°C.

Figures 6 to 10 inclusive show the change of concentrations in extraction streams of Cl^-, specific conductance, T.S., COD and ABS respectively. Higher concentration values for the first extraction are due to the use of pure DIPA which results in a smaller volume of raffinate, thus higher concentrations.

The analytical results and material balances are tabulated in Tables 7 to 11. The per cent distribution and ratios of concentration in raffinate to that in the product are also shown in these tables.

Chloride Distribution. Excluding the first extraction in which pure DIPA was used, the chloride ion distribution between the raffinate and product was not affected by the re-use of solvent. Up to the fifth extraction about 84% of the chloride was concentrated in the raffinate. Figure 6 shows the concentration change of Cl^- in the raffinate and product, with an average concentration ratio of 3.55. A product chloride content of 23 to 27 mg/l as compared to 67.3 mg/l in the feed was obtained in a single stage extraction after having used the solvent five times.

Specific Conductance (Figure 7). The distribution of ionizable matter as measured by conductivity seems to be unaffected by the re-use of solvent. A high concentration ratio of 8.0 or more for such compounds

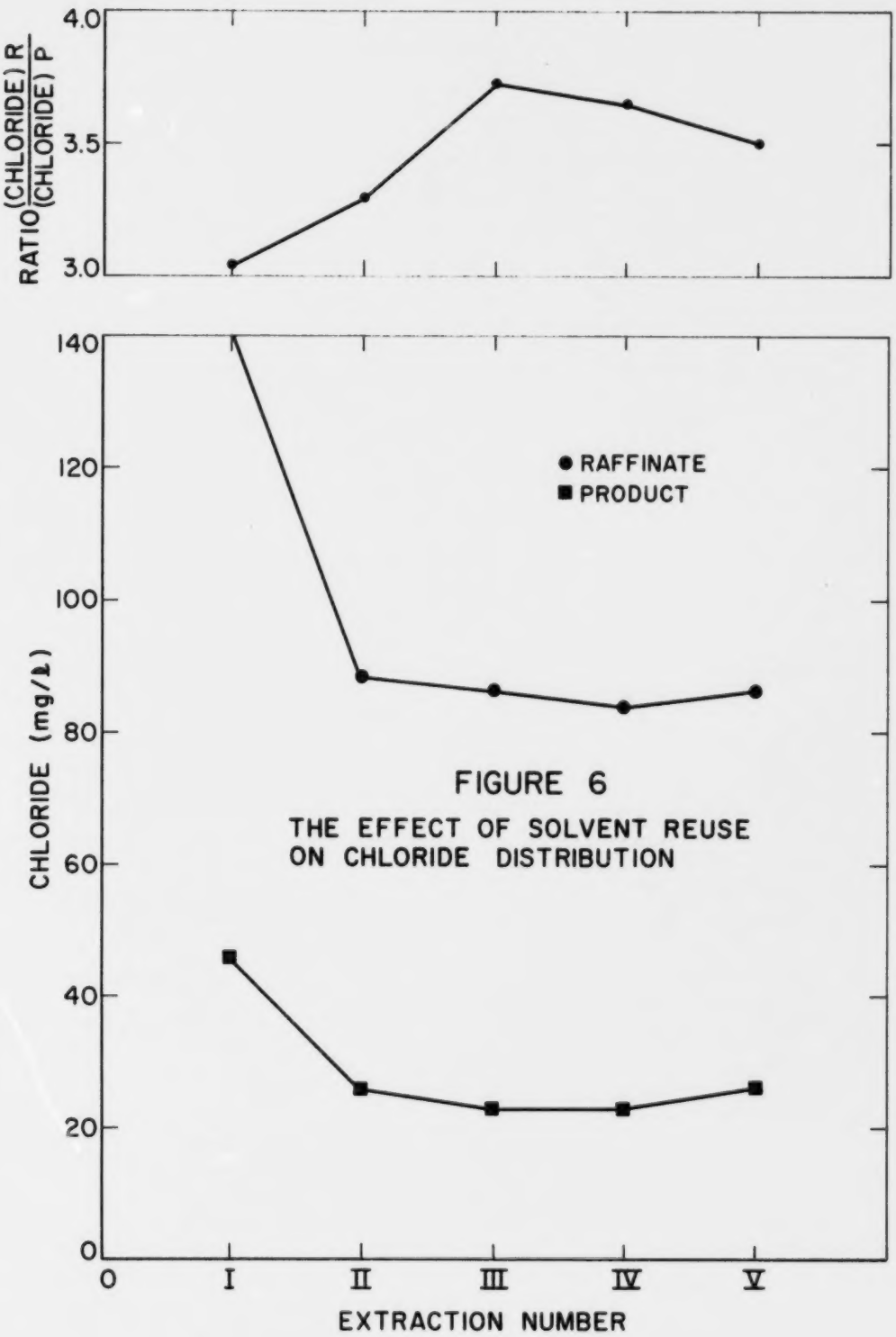


FIGURE 6

THE EFFECT OF SOLVENT REUSE ON CHLORIDE DISTRIBUTION

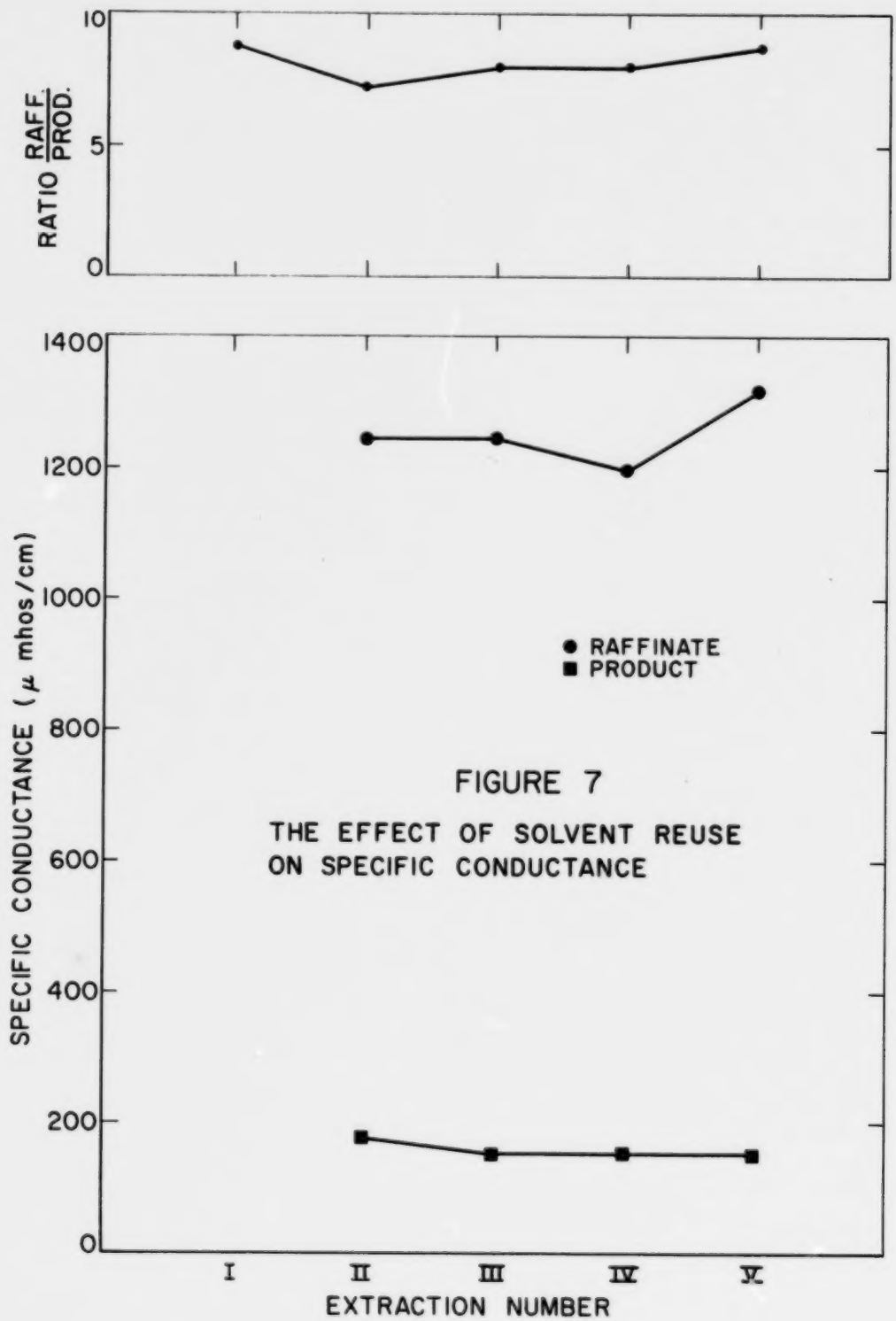


FIGURE 7

THE EFFECT OF SOLVENT REUSE ON SPECIFIC CONDUCTANCE

Table 7 - EXTRACTION I

Feed ---------- 800 ml Raffinate = 230 gm

Pure DIPA ----- 1600 gm Product = 320 gm

Solvent 1 = 1792 gm

	Chloride		COD		ABS		Sp. Cond.	T.S.		T.S. Calculated		V.S. = T.S. Prac.-F.S.Calc.	
	mg/L	mg	mg/L	mg	mg/L	mg	μ mhos/cm	mg/L	mg	mg/L	mg	mg/L	mg
Feed	67.3	35.84	113.3	90.64	6.72	5.376	813	560	448	560	448	200	160
Raffinate	140.97	32.42	219.9	50.30	0.60	0.138	2410	1588	365	1658	381	523	120.3
Product	46.06	14.74	60.5	19.36	0.32	0.103	270	140	44.8	185	59	31	9.9
Solvent	----	----	40.85	73.15	2.875	5.150	----	----	----	----	----		29.2
TOTAL		48.16		142.81		5.391		409.8		440			

Per Cent Distribution

	COD	Cl	ABS	T.S.
Feed	100	100	100	100
Raffinate	55.5	67.3	2.6	81.2
Product	21.3	32.7	1.9	10.0
Solvent	23.2	----	95.5	8.8

Ratio of Conc. $\frac{\text{raffinate}}{\text{product}}$

COD	3.63
Chloride	3.08
T.S.	11.34
Sp. Cond.	8.89

Table 8 - EXTRACTION II

Feed ---------- 800 ml

Solvent 1 ----- 1600 ml

Raffinate = 490 gm

Product = 310 gm

Solvent 2 = 1512 gm

	Chloride		COD		ABS		Sp. Cond.	T.S.		T.S. Calculated		V.S. = T.S. Prac.-F.S.Calc.	
	mg/L	mg	mg/L	mg	mg/L	mg	μ mhos/	mg/L	mg	mg/L	mg	mg/L	mg
Feed	67.3	53.84	113.3	90.64	6.72	5.376	813	560	448	560	448	200	160
Raffinate	87.94	43.02	106.8	52.33	0.48	0.234	1247	868	425.3	858		307	150.4
Product	26.52	8.22	25.5	7.91	0.52	0.161	175.8	96	29.7	121		18.3	5.7
Solvent	----	----	92.45	74.42	7.5	6.74	----	----	----	----			3.9
TOTAL		51.24		134.66		7.136			455.0				

Per Cent Distribution

	COD	Cl	ABS	T.S.
Feed	100	100	100	100
Raffinate	57.7	84	3.35	93.4
Product	8.7	16	2.25	6.6
Solvent	33.6	---	94.4	----

Ratio of Conc. $\frac{\text{raffinate}}{\text{product}}$

COD	4.18
Chloride	3.31
T.S.	9.04
Sp. Cond.	7.15

Table 9 - EXTRACTION III

Feed ---------- 656 ml

Solvent 2 ----- 1312 gm

Raffinate = 400 gm

Product = 256 gm

Solvent 3 = 1250 gm

	Chloride		COD		ABS		Sp. Cond	T.S.		T.S. Calculated		V.S. = T.S. Prac.-F.S.Calc	
	mg/L	mg	mg/L	mg	mg/L	mg	μ mhos/cm	mg/L	mg	mg/L	mg	mg/L	mg
Feed	67.3	44.15	108.4	71.11	6.72	4.408	813	560	367	560	367	200	131.2
Raffinate	86.3	34.52	100.8	40.30	0.40	0.160	1248.9	900	360	859	343	307	122.8
Product	23.0	5.89	48	12.29	0.48	0.123	154.1	124	31.7	106	27	38	9.7
Solvent	----	----	147.1	62.60	10.57	3.67	----	----	----	----	----	----	0.0
TOTAL		40.41		115.19		3.953			391.7		370		

Per Cent Distribution

	COD	Cl	ABS	T.S.
Feed	100	100	100	100
Raffinate	56.7	85	4.0	92
Product	17.3	15	3.1	8
Solvent	26.0	---	92.9	---

Ratio of Conc. $\frac{\text{raffinate}}{\text{product}}$

COD	2.1
Chloride	3.75
T.S.	7.26
Sp.Cond.	8.1

Table 10 - EXTRACTION IV

Feed ---------- 500 ml

Solvent 3 ---- 1000 gm

Raffinate = 300

Product = 200

Solvent 4 = 960

	Chloride		COD		ABS		Sp. Cond.	T.S.		T.S. Calculated		V.S. = T.S. Prac.-F.S.Calc.	
	mg/L	mg	mg/L	mg	mg/L	mg	μ mhos/cm	mg/L	mg	mg/L	mg	mg/L	mg
Feed	67.3	33.7	100.7	50.35	6.72	3.36	813	560	280	560	280	200	100
Raffinate	83.75	25.13	116.9	35.07	0.40	0.12	1200	694	208.2	825	247.5	163.6	49.1
Product	23.0	4.60	45.8	9.16	0.52	0.104	155	137.5	27.5	106.6	21.2	69.0	13.8
Solvent	----	----	207.4	52.0	15.0	3.83	----	----	44.3	----	11.3	----	37.1
TOTAL		29.73		96.23		4.054			280		280		

Per Cent Distribution

	COD	Cl	ABS	T.S. anal.	T.S. calc.
Feed	100	100	100	100	100
Raffinate	69.6	84.5	3.0	74.3	88.2
Product	18.2	15.5	2.2	10.0	7.6
Solvent	12.2	----	94.8	15.7	4.2

Ratio of Conc. $\frac{\text{raffinate}}{\text{product}}$

COD	2.55
Chloride	3.64
T.S.	5.07
V.S.	
Sp.Cond.	8.0

Table II - EXTRACTION V

Feed ---------- 370 ml

Solvent 4 ------ 739 gm

Raffinate = 230

Product = 160

Solvent = 680

	Chloride		COD		ABS		Sp. Cond.	T.S.	
	mg/L	mg	mg/L	mg	mg/L	mg	μ mhos/L cm	mg/L	mg
Feed	67.3	24.9	100	37	6.72	2.45	813	560	207.2
Raffinate	86.4	19.87	96.4	22.1	0.32	0.074	1350	854	196.4
Product	27.45	4.12	177.0	26.5	0.44	0.066	153	36	5.4
Solvent	----		263	25.6	19.5	2.17	----	----	----
TOTAL		23.99				2.31			201.8

holds well during the extractions III, IV and V. Products from the last three extractions had a sp. conductance of 155 μmhos/cm as compared to 813 μmhos/cm for the sewage water sample.

Total Solids Distribution (Figure 8). The high percentage of the T. S. concentrated in the raffinate and its low value in the product (96-140 mg/l) is not affected by the re-use of solvent. The concentrations of T.S., as found experimentally and as calculated from specific conductance, agree within 5 to 10%. The average concentration ratio of a single stage extraction is found to be between 7 and 8 which is much higher than that found for the Cl^- and almost as high as the ratio of specific conductance.

Organic Matter Distribution "COD" (Figure 9). The results indicate that 55 to 58% of the organic load in the sewage sample is concentrated in the raffinate. The most favorable distribution was obtained in the second extraction with 8.7% of total organics in the product resulting in a COD of 25 mg/l. The per cent of organics contaminating the product increases by solvent re-use resulting in higher COD values and a lower selectivity. The COD concentration in the solvent increased as it was re-used. The COD in the solvent was calculated by difference, since the analytical values were higher than indicated by material balance. The difference between the analytical and calculated COD concentration in the solvent may be due to some amine chemically bound to an organic contaminant that is soluble in

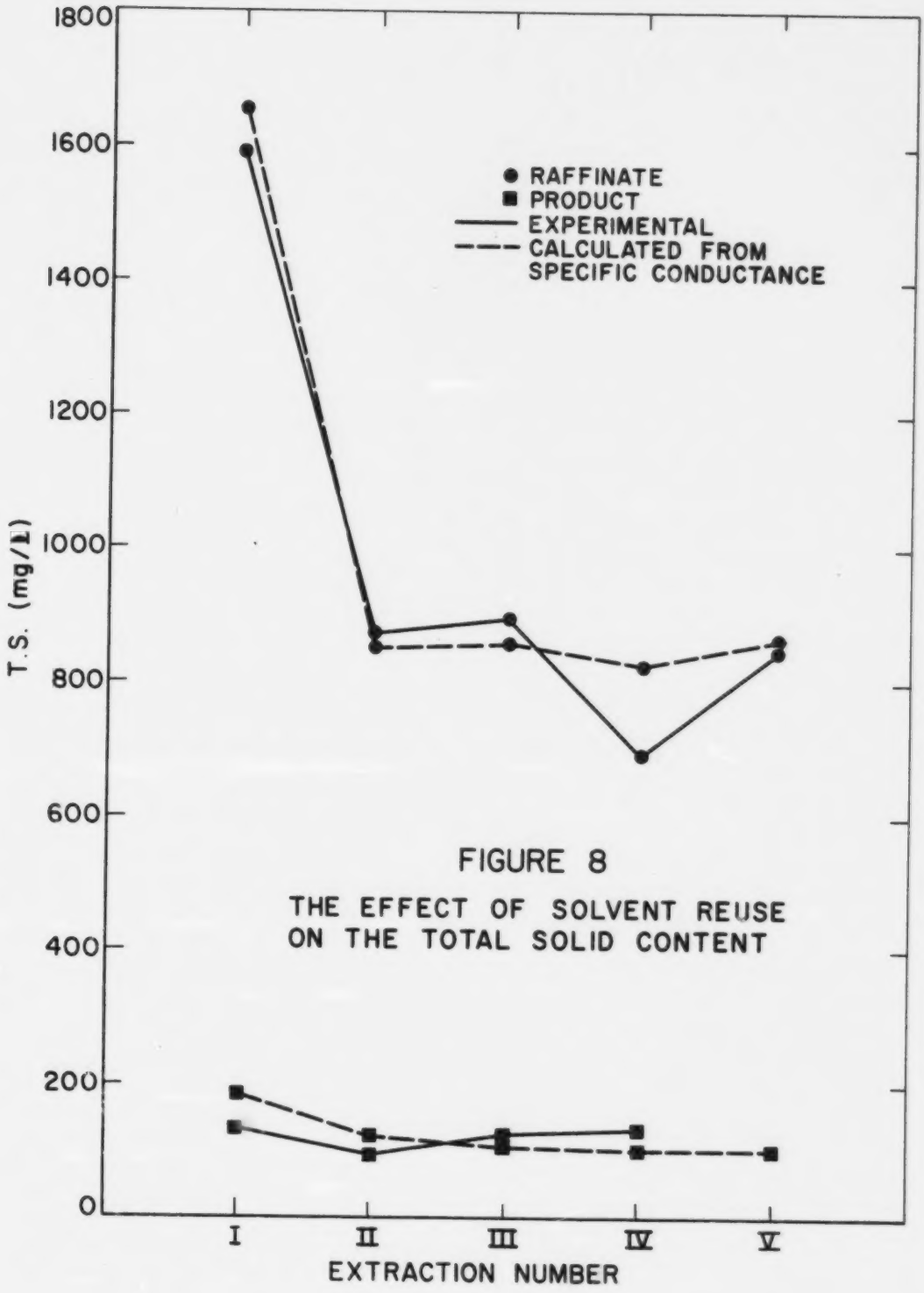


FIGURE 8

THE EFFECT OF SOLVENT REUSE ON THE TOTAL SOLID CONTENT

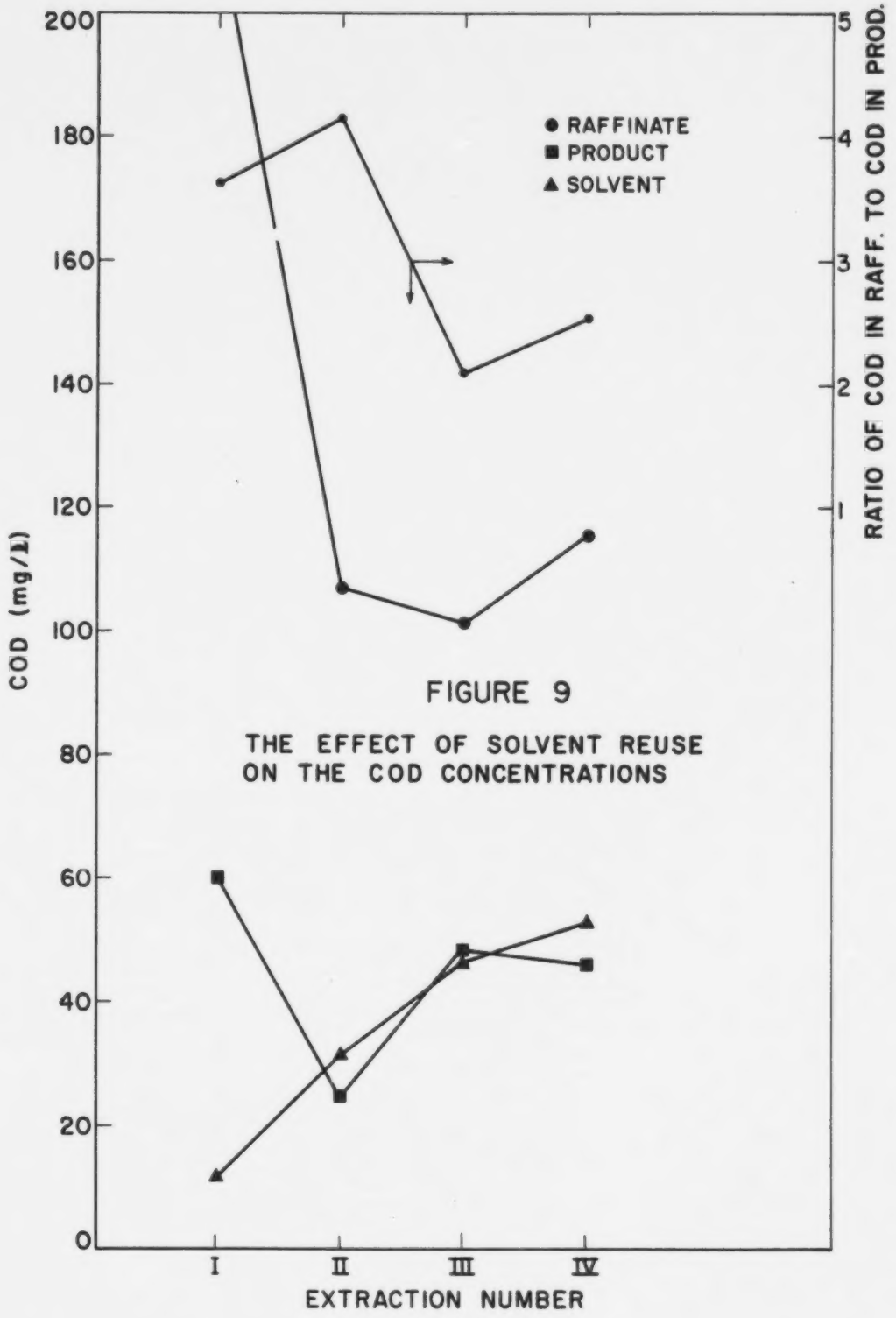


FIGURE 9

THE EFFECT OF SOLVENT REUSE ON THE COD CONCENTRATIONS

the solvent phase.

ABS Distribution (Figure 10). The concentration of ABS in the solvent phase increased from 2.87 to 19.5 mg/l when the solvent was re-used five times, without any increase of ABS concentration in the raffinate or product.

It seems that the solvent can be re-used many times without affecting the quality of the product with respect to ABS concentration in spite of the fact that ABS concentration did build up in the solvent phase.

The solvent re-use is apparently limited by the build up of the organic contaminants in the solvent phase. The life of the solvent before rectification could be increased by a pretreatment to remove some of the organic material. This will be discussed under the continuous counter current extraction of sewage secondary effluents.

HETEROGENEOUS EQUILIBRIUM OF INORGANIC IONS IN THE WATER-AMINE SYSTEM

In previous publications Davison and Hood (3) (5) (6) discussed the factors influencing the ability of a solvent to extract and release water over a narrow temperature interval, but to be effective a solvent must not only extract water from saline solutions but do so selectively. Of the compounds tested as possible solvents, the secondary and tertiary amines were found to have the best

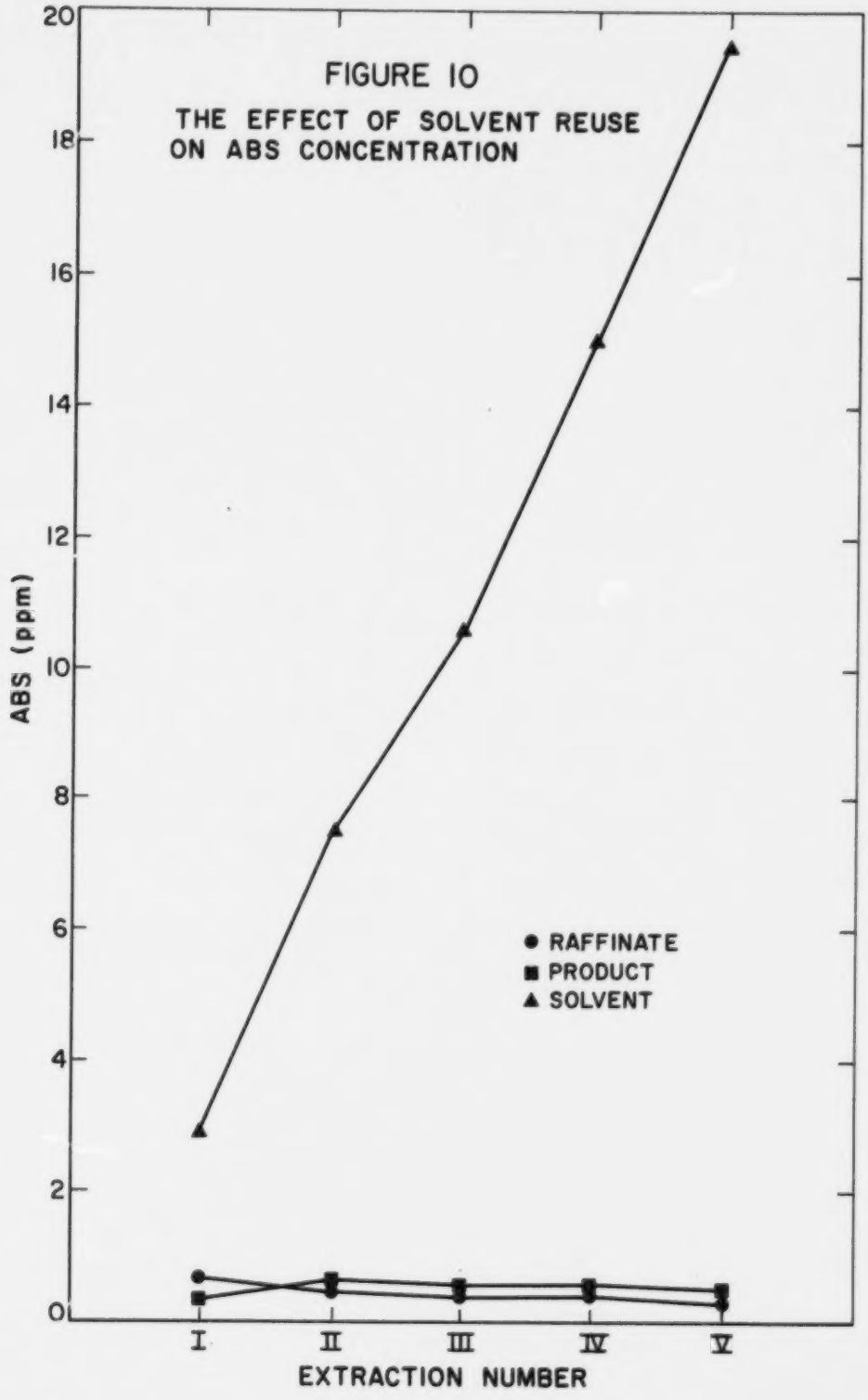


FIGURE 10
THE EFFECT OF SOLVENT REUSE
ON ABS CONCENTRATION
ABS (ppm)
20
18
16
14
12
10
8
6
4
2
0
RAFFINATE
PRODUCT
SOLVENT
I
II
III
IV
V
EXTRACTION NUMBER

selectivities. The object of this study is to determine the selectivities of DIPA and mixtures of triethylamine (TEA) and methyldiethylamine (MDEA) with respect to the different inorganic ions most commonly found in sewage secondary effluents.

Since we are interested in the quality of water which may be separated from a solvent in contact with a water of given concentration, selectivities are expressed on a solvent free basis;

$$\text{Selectivity} = \frac{\dfrac{\text{Wt. fraction ion}}{\text{Wt. fraction salt + Wt. fraction water}}\ \text{water phase}}{\dfrac{\text{Wt. fraction ion}}{\text{Wt. fraction salt + Wt. fraction water}}\ \text{solvent phase}}$$

$$= \frac{(\text{Wt. fraction salt + Wt. fraction water})S}{(\text{Wt. fraction salt + Wt. fraction water})W} \times \frac{(\text{Wt. fraction ion})W}{(\text{Wt. fraction ion})S}$$

$$\therefore K_{ion} = \frac{100 - \text{Per Cent Amine in Solvent Phase}}{100 - \text{Per Cent Amine in Water Phase}} \times \frac{W}{S}$$

where $\frac{W}{S}$ represents the ratio of the ion concentration in the water to that in the solvent phase.

The amine content of both phases is determined by titration. The sample is injected into an ampoule containing a known quantity of HCl. The quantity of solution added is determined by weighing, and the contents are back-titrated with standard NaOH solution.

Equilibrium of Sodium Chloride: Water: Amine System

The concentration of ions in both phases was determined by conventional methods and radioactive tracing of labeled ions in solutions.

Radioactive Tracing. The solvent and salt solutions of gradient strengths were placed in rubber-capped ampoules. Three identical mixtures, i.e. the same ratios of water to solvent, were made at each salt concentration. One was labeled with Na^{22} another with Cl^{36} and one was unlabeled. The ampoules were placed in a rack and rotated in a constant temperature bath for at least 24 hours. The phases to be analyzed were withdrawn through a hypodermic needle while the samples were kept at the same temperature in the bath. The amine content of both phases was determined by titration of the unlabeled vials. The sodium and chloride contents of both phases was determined by placing a small sample of the water and solvent from the ampoules labeled with Na^{22} and Cl^{36} in planchets to which drops of NaOH have been added before drying under a lamp. The planchets were then counted and the ratio of counts in both phases determined. More reproducible counts were obtained by placing circles of lens paper in the planchets, moistening with 0.5 M sucrose solution and drying before introducing the sample. This was believed to minimize geometrical differences.

Conventional Analysis. The solvent and salt solutions of gradient strengths were placed in separatory funnels and equilibrated in a constant temperature bath for at least 24 hours, then the phases were separated, weighed and stored at 4°C to prevent any loss of amine. The amine content of both phases was determined by titration. Samples from each phase were weighed, distilled free of amine, and diluted to a

known volume. The prepared samples were then analyzed for Na^+ by flame photometry and for Cl^- by $AgNO_3$ titration. The concentrations of Na^+ and Cl^- in both phases were then calculated on a solvent free basis.

The equilibrium constant for salt was calculated as the geometric mean of that for the Na^+ ion and that for the Cl^- ion.

$$K_{salt} = (K_{Na} \times K_{Cl})^{\frac{1}{2}}$$

In Figure 11 the equilibrium constant for sodium chloride was plotted as a function of mol per cent water in the solvent phase. The points on the lower curve represent data obtained for secondary and tertiary amines and mixtures of tertiary amines by the radioactive tracing technique at different temperatures. The upper curve represents the data obtained for a 2:1 mixture of MDEA and TEA by conventional analysis at different temperatures and salt concentrations. Results obtained by the two methods agree fairly well for a water content of 60-80 mol per cent, while selectivities as measured by radioactive tracing are less than those obtained from conventional analysis for a water content below 55 mol per cent.

From theoretical considerations, one would expect the sodium chloride selectivity to be primarily a function of the water content and the salt content and to a lesser extent the distribution of the amine ion through its effect on the ionic strength. The degree of the amine

hydrolysis determines the extent of the imbalance between sodium and chloride ions. The ratio of $K+/K-$ is strongly affected by the salt content and is greatest at low salt content. It varies for different amines depending on the amine solubility but the $\sqrt{K+K-}$ is always the same for different amines. For secondary and tertiary amines this ratio is approximately 1 except in very dilute solutions.

The dramatic effect of water content and the lack of any influence of salt content on the equilibrium of secondary and tertiary amines is clearly seen from the data plotted in Figure 11.

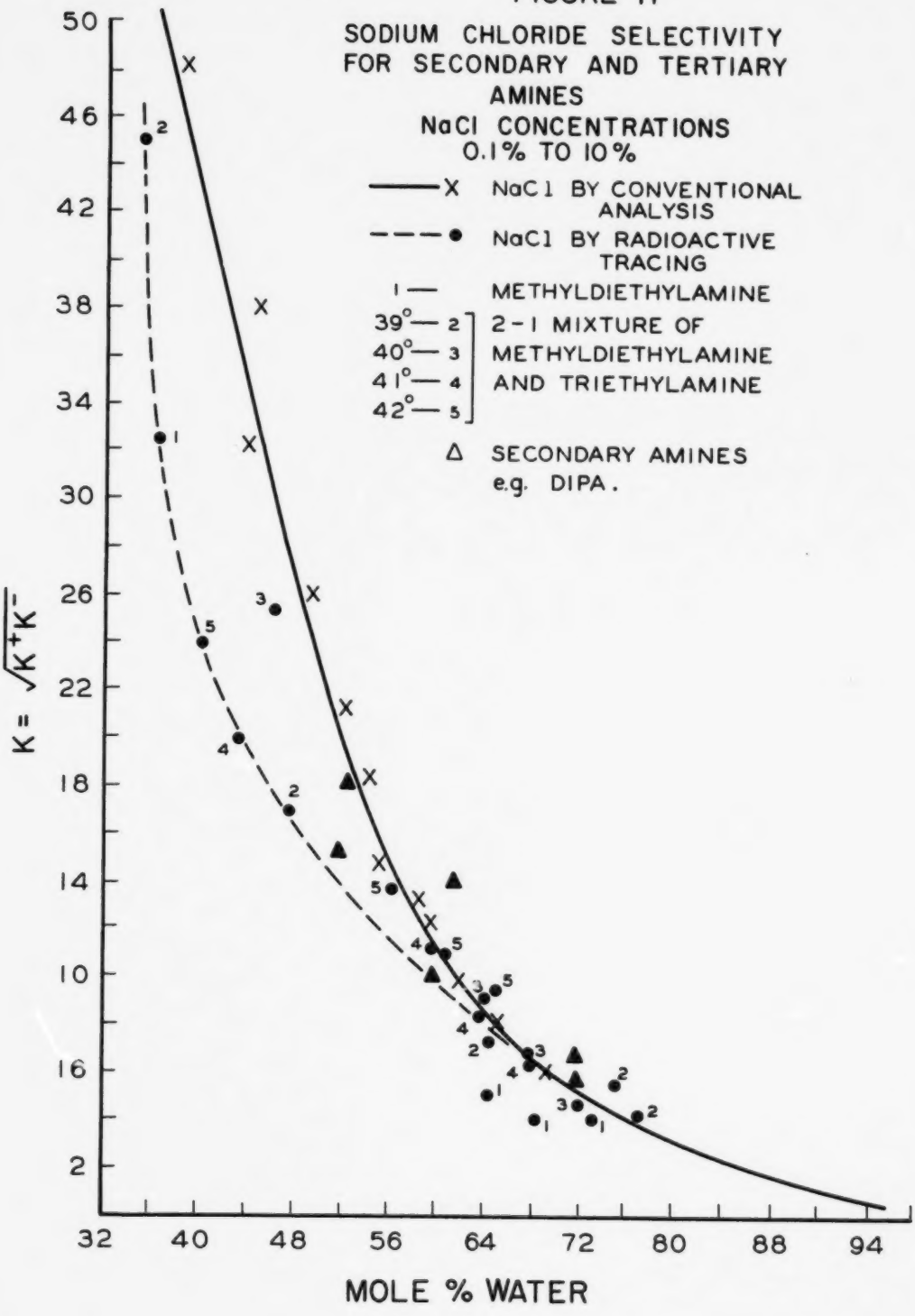
Equilibrium of Calcium Ion in Sodium Chloride:Water:Amine System

When solutions of calcium chloride are mixed with amines, calcium hydroxide is precipitated. This limited the possible concentrations of $CaCl_2$, to be studied, to those below 1500 mg/l. Furthermore it was found that a concentration of $CaCl_2$ as low as 400 mg/l precipitates the carbonate since the amine contains CO_2 absorbed from the air. Gradient strengths of $CaCl_2$ solutions were prepared using freshly boiled distilled water, then mixed with distilled DIPA collected under nitrogen. Two identical mixtures were made at each salt concentration. One was labeled with Ca^{45} and the other not. The solutions in rubber-capped ampoules were placed in a rack and rotated in a constant temperature bath for 24 hours. The amine content of both phases was determined by titration and the Ca content of the water

FIGURE 11

SODIUM CHLORIDE SELECTIVITY FOR SECONDARY AND TERTIARY AMINES

NaCl CONCENTRATIONS 0.1% TO 10%



phase was titrated with standard EDTA using the unlabeled samples. The Ca content of both phases was determined by counting the labeled sample, as explained under Na and Cl.

The equilibrium data of calcium in the NaCl-DIPA system at two different temperatures were given in the following Table 12 and plotted in Figure 12. In the same figure the equilibrium data for NaCl was plotted. For a water content of 55 to 70 mol per cent the Ca selectivity was higher than that of NaCl, and not as sensitive to water content. It is of interest to note that by extrapolating the two curves they intersect at the consulate composition, nearly 90 mol per cent water, where K is supposed to be equal to unity.

Equilibrium of the Nitrate Ion in Sodium Chloride:Water:Amine System

Standard solutions of KNO_3 containing 50 to 1000 mg/l NO_3^- with 0, 0.1 and 1% NaCl, were equilibrated at different temperatures with DIPA and a 1:1 mixture of MDEA and TEA. The two phases were then separated and stored at 4°C.

It was found that the amine interferes with the NO_3 analysis using the brucine sulphate method. Samples of both phases were weighed, distilled free of amine, then diluted to a known volume before analysis for the NO_3^- content.

Results of these tests are given in Table 13. The ratio K for the DIPA is between 1.00 and 1.166 for NO_3^- content up to 800 mg/l.

FIGURE 12

SELECTIVITY OF CALCIUM AND SODIUM
IN AMINE-WATER SYSTEM

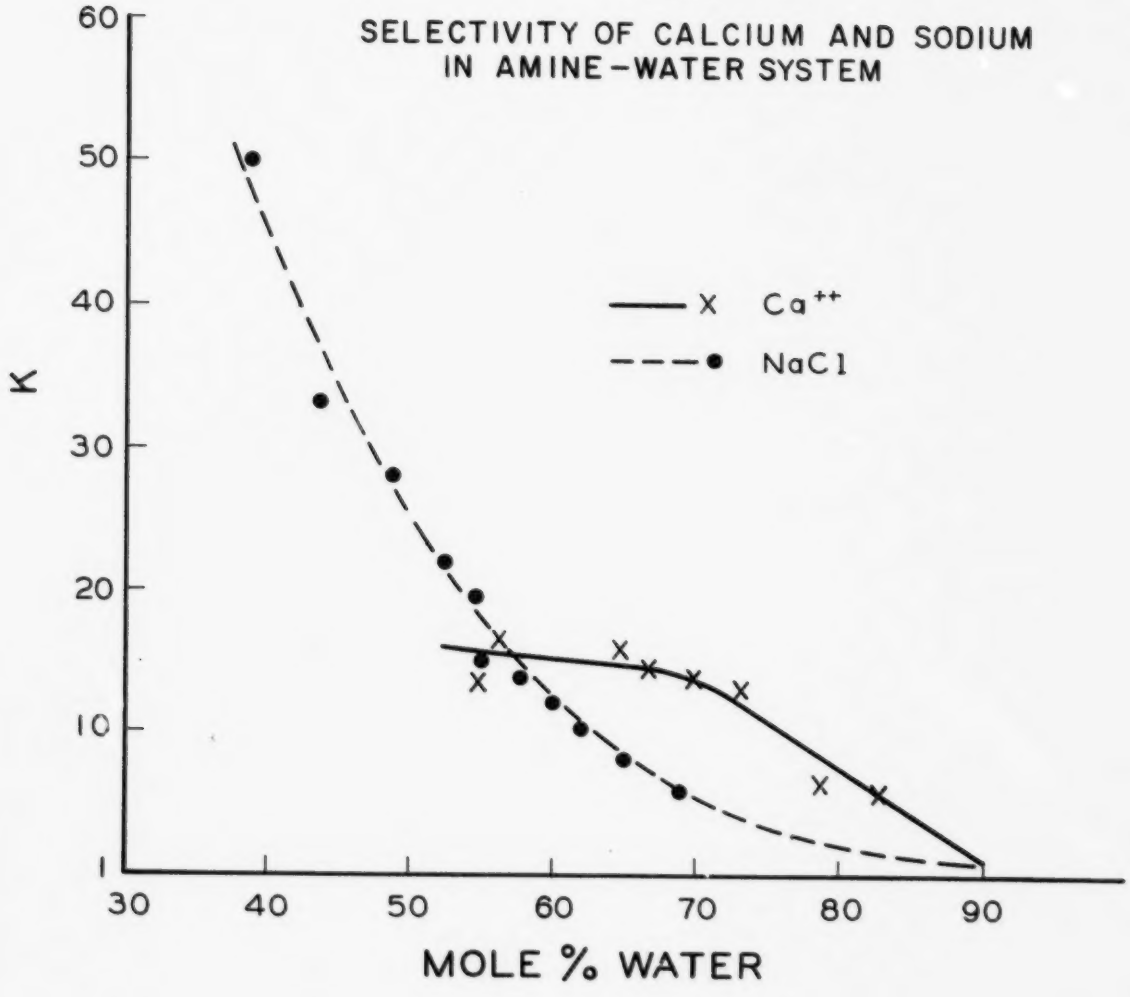


Table 12

Heterogeneous Equilibrium of Calcium Ion

in Diisopropylamine - Water - Sodium Chloride

Temp. °C	Solution mg/l Ca^{++}	% NaCl	Mg/l Ca^{++} in Solvent ph.	Mg/l Ca^{++} in water ph.	Ratio of Ca^{45} $\frac{W}{S}$	Selectivity K
33.5	595	0		442	45.9	14.5
	395	0	69.8	467	36.7	11.6
	200	0		243	40.9	13.1
	595	0.5		712	51.3	14.4
	395	0.5	66.7	358	46.2	13.2
	200	0.5		245	52.1	14.9
	560	1.0		702	60.6	15.7
	400	1.0	64.5	477	62.1	16.3
	200	1.0		239	62.0	16.4
	465	3.0		868	72.1	12.6
	390	3.0	54.6	458	71.7	13.4
	200	3.0		222	69.7	13.6
28.5	520	0		602	11.0	
	395	0	82.7	478	10.1	5.6
	200	0		250	11.0	
	520	0.5		620	14.1	
	395	0.5	78.	472	14.8	6.5
	200	0.5		232	15.1	

Table 13

Equilibrium of the Nitrate Ion in Sodium Chloride:

Water:Amine System

Solvent	Standard Solution % NaCl	Standard Solution mg/l NO_3^-	Water Phase mg/l NO_3^{-*} (W)	Solvent Phase mg/l NO_3^{-*} (S)	Ratio K = W/S
DIPA	0	95	99.0	99.5	1.00
DIPA	0	49	51.4	56.8	0.905
DIPA	2	43	56.4	55.7	1.013
DIPA	0	186	217	195	1.166
DIPA	0.1	217	243	210	1.122
DIPA	0	560	650	550	1.160
DIPA	0.1	790	705	620	1.137
DIPA	1.0	560	700	550	1.270
1:1 MDEA,TEA	0	1100	1220	802	1.524
1:1 MDEA,TEA	0.1	910	1120	717	1.566
1:1 MDEA,TEA	0	475	525	455	1.153
1:1 MDEA,TEA	0.1	420	468	384	1.218
1:1 MDEA,TEA	0	155	152	173	0.874
1:1 MDEA,TEA	0.1	180	155	163	0.951

*Calculated on solvent free basis.

When a 1:1 mixture of MDEA and TEA was used K seems to be dependent on the concentration of the NO_3^- going up to 1.56 for 1000 mg/l NO_3^-.

The very low selectivity of the NO_3^- ion can't be explained. It seems to be slightly more soluble in the water phase, but not enough to effect a separation in a reasonable number of solvent extraction stages.

Equilibrium Distribution of Organic Contaminants in Sewage Water-Amine System

Batch extraction of sewage samples indicated a remarkable difference between the distribution of the organic matter, as measured by COD, and V.S. Table 14 shows the per cent distribution of COD, Cl^- and V.S. for the extraction of sewage samples 4 and 5. The V.S. test was found to be unreliable, but still the difference between COD and V.S. seemed significant. In Table 15 is given the ratio of COD/V.S. for the process streams in the batch extraction of samples 4 and 5. This indicates that the organic materials which prefer the solvent phase have a higher COD value per unit weight than the organics which prefer the water phase and are concentrated in the raffinate or contaminate the product. It is likely that most of the organic matter that stays in the solvent phase is made up of fats, hydrocarbons and ABS-like materials, while the highly oxygenated compounds stay in the water phase due to higher water solubility.

Table 14

Distribution of Organic Matter, Cl^- and V.S.

	% COD		% Cl		% V.S.	
	Sample 4	Sample 5	Sample 4	Sample 5	Sample 4	Sample 5
Raffinate	49	52.6	81.4	87	75.7	74.2
Product	9	10.1	18.6	13	12.9	14.3
Solvent	42	37.3	----	--	11.4	11.5

Table 15

Ratio of $\frac{COD}{V.S.}$ in Process Streams

	Sample 4		Sample 5	
Feed	$\frac{110.5}{162.5}$ = 0.68		$\frac{87.7}{140}$ = 0.625	
Raffinate	$\frac{130.5}{282.0}$ = 0.462		$\frac{132}{196.3}$ = 0.667	
Product	$\frac{25.4}{52.8}$ = 0.482		$\frac{34.6}{52.5}$ = 0.662	
Solvent	$\frac{38.2}{14.8}$ = 2.581		$\frac{.80}{24.9}$ = 3.226	

Tritium Labeling of Organic Matter from Sewage Effluents

The preparation of tritium-labeled material from sewage effluents was then proposed as an alternate method to study the heterogeneous equilibrium of the organic fraction between the raffinate, extract, solvent, and product water. This method would have the additional feature of eliminating the interference of any traces of amine in the solvent extraction streams.

Tritium-labeled organic matter was prepared from sewage samples 6 and 8. The sample was first acidified with one per cent HCl and nitrogen gas was blown through for five hours to get rid of the bicarbonate. The sample was then placed in a freeze-drying apparatus for four days until it was completely dry. The dry solid matter from each sample was treated with tritium gas in the Wiltzbaugh reaction for one hundred hours, a period thought to give a high specific activity to the tritium-labeled organic matter without causing much radiation damage to the parent organic compounds. Excess tritium was swept out, then the treated samples were suspended in distilled water and freeze-dried to clean up the non attached and readily labile tritium. The tritium-labeled solid matter was weighed, dissolved in distilled water, and mixed with a high speed mixer (16,000 RPM). Complete dissolution was not obtained, since some of the original solid matter was colloidal. These solutions were used to spike the sewage samples from which they were prepared, then the spiked solution was extracted

with twice its weight of DIPA at 35°C and the product separated at 50°C. The solvent phase was distilled and the residue diluted to 100 ml. The extraction streams, raffinate, product, and solvent residue were analyzed for tritium count, COD, and V.S.

The scintillator was prepared by dissolving four gms of PPO (2, 5 diphenyloxazole) and 0.1 gm POPOP (1,4-bis-2(5-phenyloxazoyl)-benzene) in 800 ml toluene and 200 ml ethanol. Ten ml portions of the scintillator were placed in the vials and a sample of 0.1 ml was counted for ten minutes in a Packard Tri-Carb Liquid Scintillation Spectrometer.

The stock spike solutions were concentrated and colored. To check if the color would cause any quenching of the scintillation system, duplicate samples of different dilutions were counted and were found to exhibit no color quenching.

The distribution of organic matter in solvent extraction streams as found from tritium counting is compared to COD distribution in Table 16 and V.S. distribution in Table 17. The tritium counting showed a much higher per cent of organics in the raffinate and a much lower per cent in the solvent, as compared to the per cent distribution calculated on the basis of COD analysis. This indicates that organic matter that prefers the solvent phase is colloidal in nature and is the part that did not dissolve in water after tritium labeling. No agreement between tritium counting distribution and V.S. distribution could be found. The tritium counting method was found to have the following disadvantages:

Table 16

DIPA Extraction of Sewage Sample

Spiked with Tritium-labeled Solution

	Tritium Counting % distribution	COD % distribution
Raffinate	74	50
Product	12.3	15
Solvent	13.7	35

Table 17

Distribution of Organic Matter in the Solvent

Extraction Streams of Spiked Sewage Samples

	Sample 1 % distribution		Sample 2 % distribution	
	Tritium Counting	V.S.	Tritium Counting	V.S.
Raffinate	68	82.0	67	70.2
Product	13.3	8.0	19	9.0
Solvent	18.7	10.0	14	20.8

1. The selectivity of different organic materials for tritium can vary widely resulting in high counts in one phase and a low count in the other.
2. The nature of organic compounds is different from one sewage sample to the other, so it is necessary to prepare tritium labeled solid matter from each sewage sample.
3. The tritium labeled solid matter prepared from sewage samples does not go back in solution completely even under severe mixing conditions.

CONTINUOUS COUNTERCURRENT SOLVENT EXTRACTION OF SECONDARY EFFLUENTS

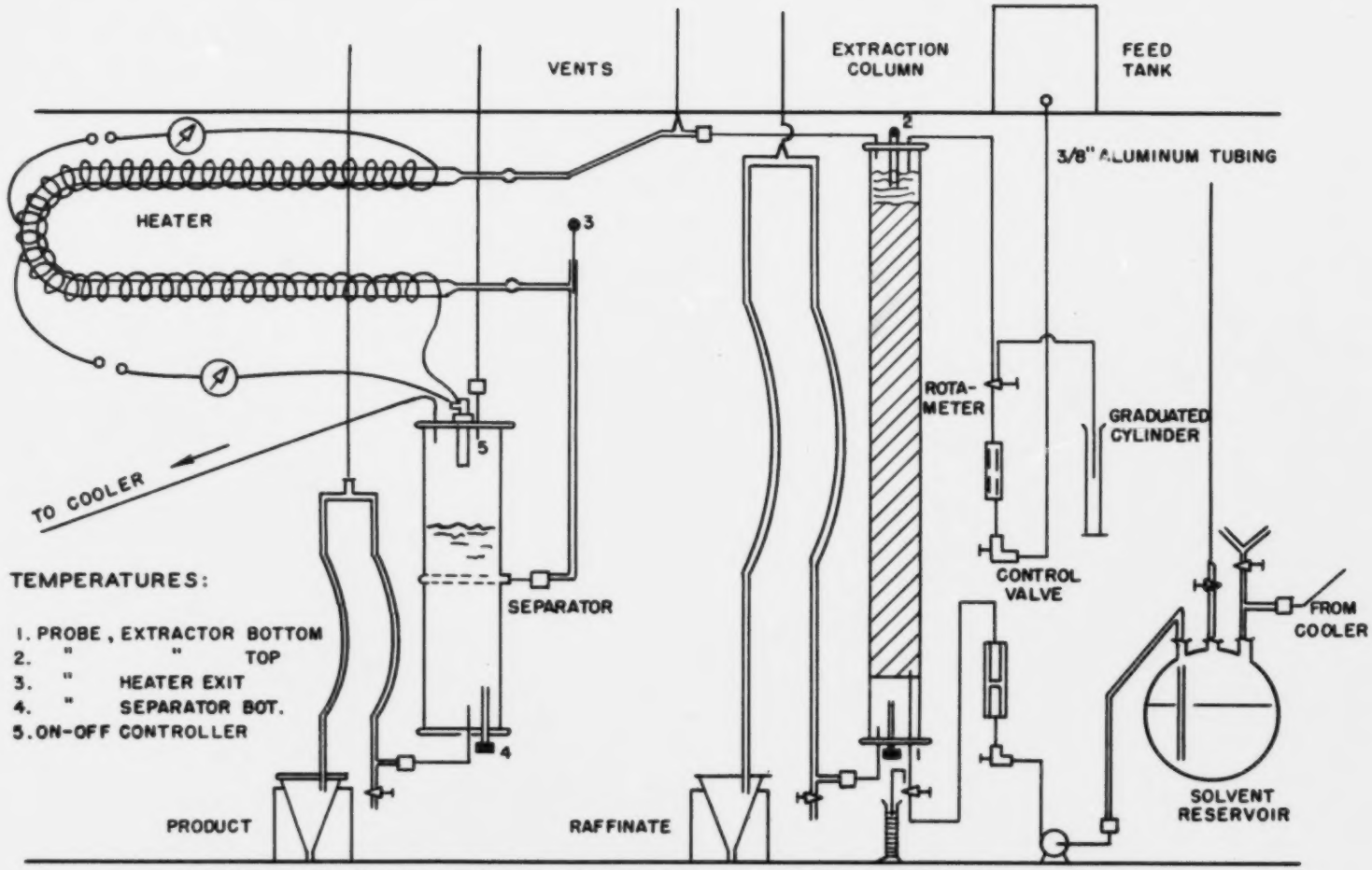
The organic contaminants selectively removed by the solvent were found to have a high COD value per unit weight as compared to those preferring the water phase. The detergent ABS was found to be chemically bound in the solvent phase as an amine complex.

The re-use of solvent in five consecutive batch extractions showed that the organic matter contaminated the solvent resulting in a high COD value of the product.

A continuous extraction unit was then built to study the number of cycles the solvent could withstand before the quality of the product would be affected by solvent contamination.

A flow sheet of the continuous solvent extraction laboratory unit is shown in Figure 13. The extraction column is a 2" glass pipe 6 ft. high of which 4.5 ft. are packed with $\frac{1}{4}$" glass Rasching rings. Single flow lines are 3/8" aluminium tubing. Vents are 2 mm. glass capillary tubing. Double lines are glass tubing of different diameters depending on the flow expected. The solvent reservoir is a 3-neck round bottom flask connected to the solvent pump. The solvent flows through a st.st. needle valve and a rotameter before entering the extractor just above the bottom of the packing. The heater is a glass U-tube wrapped with two band electric heaters which are regulated by powerstats and an on-off regulator immersed in the top of the separator. The separator consists of two one foot by three inches glass sections

FIGURE 13



CONTINUOUS SOLVENT EXTRACTION OF SECONDARY EFFLUENTS

separated by a polyethylene divider. The cooler is a multiple tube glass heat exchanger in which cooling water circulates around the outside of the tubes, through a 200 gallon cooling tank where it is cooled by a refrigerant coil and back to the cooler. The solvent overflows from the separator to the cooler tubes by gravity and back to the solvent reservoir.

The temperature at the top of the extractor is controlled by regulating the temperature of the cooling water, which determines the temperature of the solvent leaving the cooler and entering the bottom of the extractor.

Steady state conditions obtained in a trial run:

Flow of feed	=	4.65	litres/hr.
Flow of solvent	=	12.356	litres/hr.
Flow of product	=	3.08	litres/hr.
Flow of raffinate	=	2.077	litres/hr.

Temperatures:

bottom of extractor	=	32° C
top of extractor	=	33° C
exit of heater	=	55° C
cooling water	=	23° C

Material balance: basis 1 hour.

Amine in product	$= \frac{3.08 \times 5}{100 \times 0.7}$	=	0.22 litres.
Amine in raffinate	$= \frac{2.077 \times 10}{100 \times 0.7}$	=	0.297 litres.
Water in product	= 3.08 - 0.22	=	2.86 litres.
Water in raffinate	= 2.077 - 0.297	=	1.78 litres.
Total - - - - - - - - - - - - - - - -			4.64 litres.

The water feed was tap water and the conditions of flow given above represent the limiting flow the equipment can handle just before flooding occurred. The material balance was calculated assuming 5% amine in product and 10% in the raffinate and a sp. gr. of 0.70 for the pure DIPA. The holdup of the equipment was found to be as follows:

Volume of extractor and heater	=	2.1 litres.
Volume of separator	=	3.0 litres.
Volume in cooler	=	0.5 litres.
Total holdup in the system	=	5.6 litres.

CONTINUOUS EXTRACTION OF SEWAGE SAMPLE NO. 10

The sewage water sample was filtered through a continuous filter under pressure using Whatman No. 5 filter paper. About 20 gallons of the filtered sample was placed in the feed tank, and a sample was analysed periodically for COD. Pure re-distilled DIPA was used for the extraction and the column was operated with the water as the continuous phase and the amine as the dispersed phase. Samples of the raffinate and product were collected every hour. Each sample was distilled separately to recover the bulk of the amine, then 500 ml. of each was redistilled to remove the last traces of the amine. All samples were analysed for COD, ABS, NO_3^-, PO_4^{---}, Cl^-, V.S., T.S. and conductivity. A sample of the used solvent was analysed for COD and ABS.

Run 1:

After two hours of operation, flooding of the column occurred,

as indicated by rising of the interface at the top of the column, and a solvent interface moving down towards the bottom. This took place several times, and the flow had to be reduced whenever flooding occurred, till at the end of eight hours of operation the flow rates were down to 2.0 litres/hr. of water feed and 7.4 litres/hr. of solvent. This is less than half the original capacity.

The volume of the sewage water passed through the continuous extraction unit during 8 hours of operation was estimated to be about 22 litres. The volume of the solvent recycled in the system was estimated to be approximately 5 litres. From the flow rates it was calculated that the solvent was re-cycled about 14 times to extract 4.4 times its volume of sewage water.

Figures 14 a, b, and c show the change of conductivity and T.S., Cl^-, and COD of both the raffinate and product, respectively.

Table 18 is a material balance over samples 4, 5, 6 and 7. The per cent distribution of different impurities is also given.

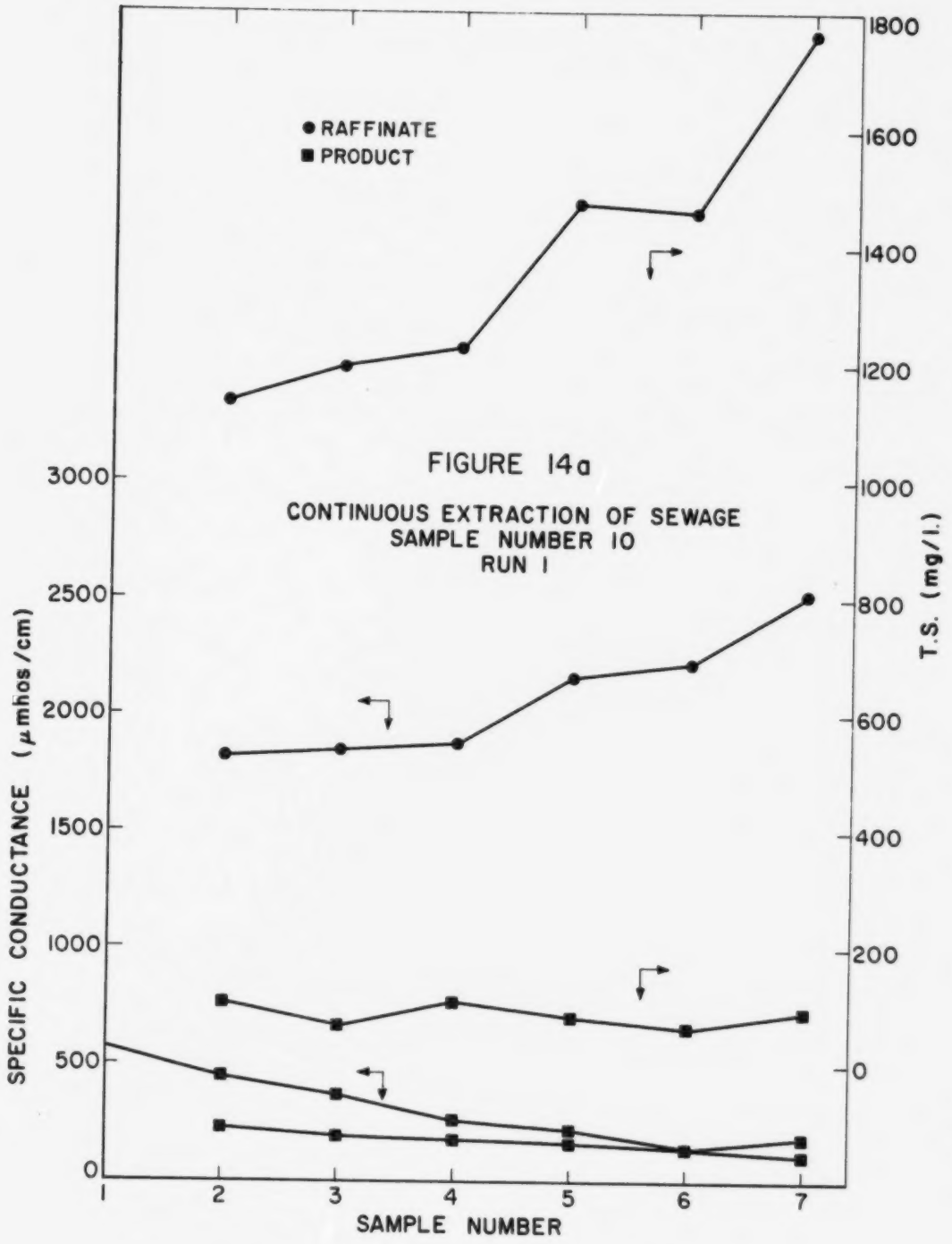


FIGURE 14a

CONTINUOUS EXTRACTION OF SEWAGE
SAMPLE NUMBER 10
RUN 1

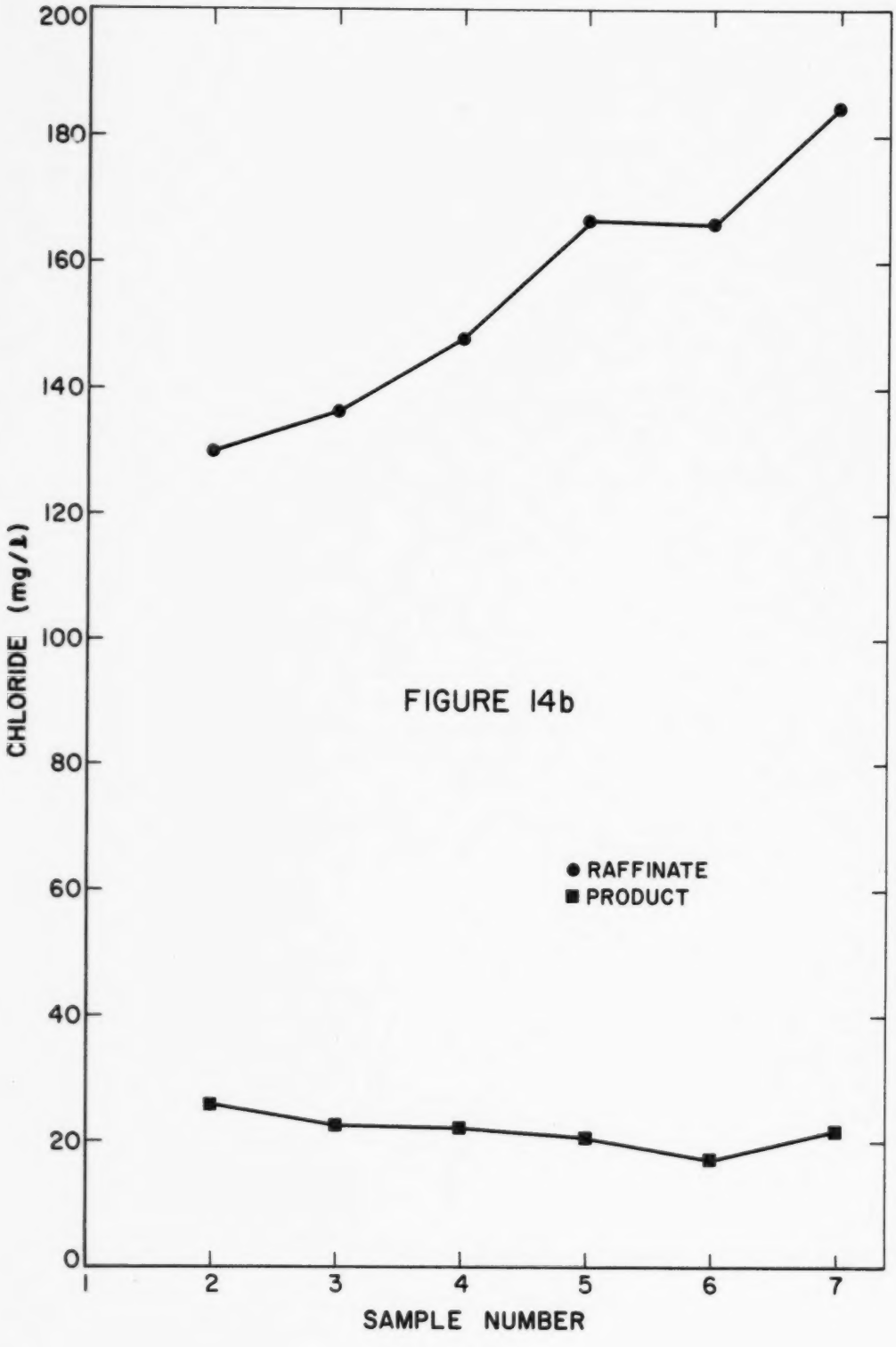

200
180
160
140
120
100
80
60
40
20
0
CHLORIDE (mg/ℓ)
1
2
3
4
5
6
7
SAMPLE NUMBER
● RAFFINATE
■ PRODUCT

FIGURE 14b

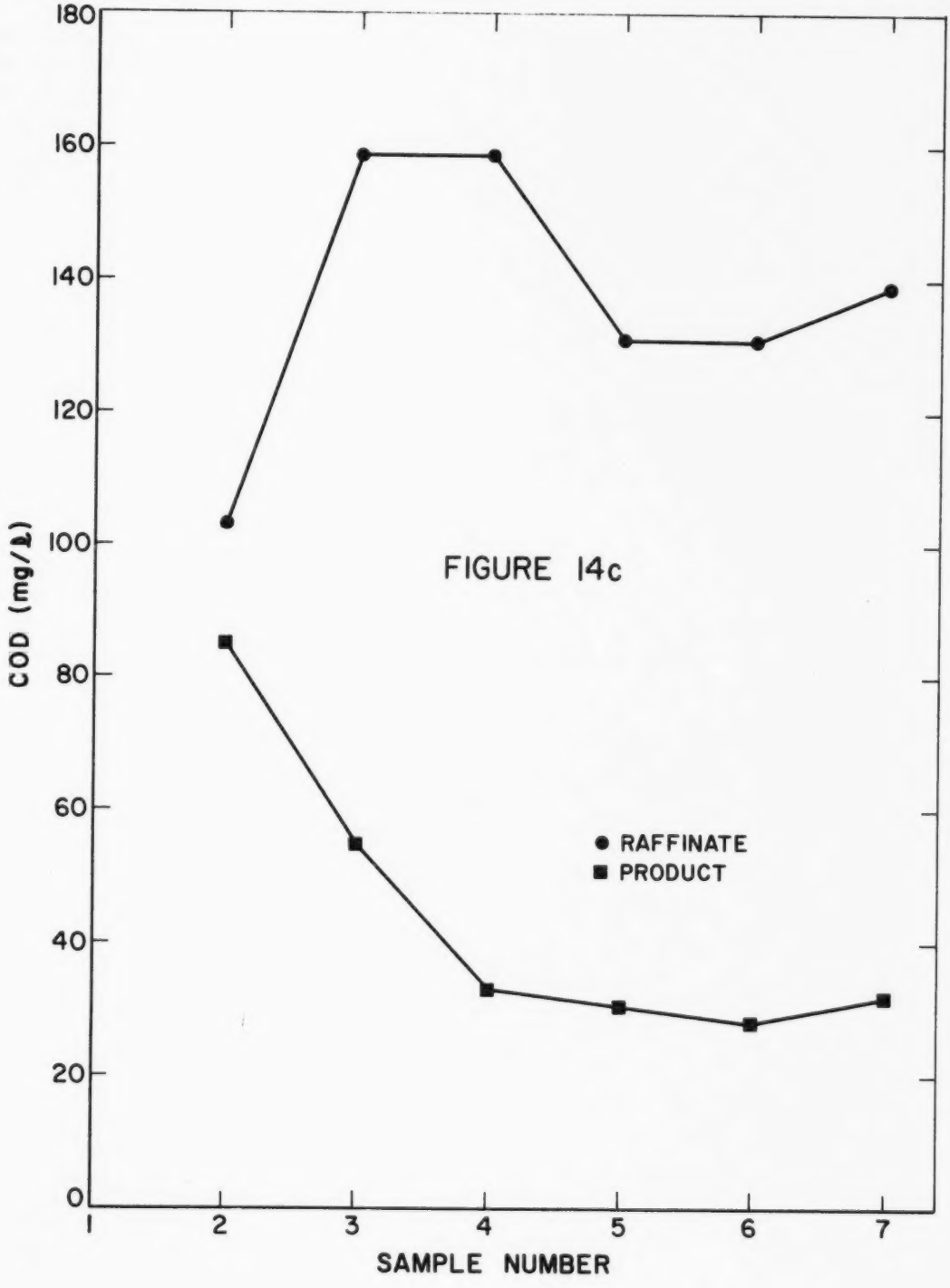

180
160
140
120
100
80
60
40
20
0
COD (mg/L)
1
2
3
4
5
6
7
SAMPLE NUMBER
RAFFINATE
PRODUCT

FIGURE 14c

Table 18

Average Material Balance and Per Cent Distribution of Contaminants (Run 1)

	Weight		COD		Cl^-		ABS		PO_4^{---}		T. S.	
	gms.	%	mg	%	mg	%	mg	%	mg	%	mg	%
Feed	7965	100	677	100	553.4	100	31.4	100	299.4	100	4793	100
Raffinate	3025	38	423	62.5	504.2	83.3	0.82	2.6	138.4	60.3	4177	88.1
Product	4940	62	153	22.6	101.3	16.3	4.55	14.5	2.97	1.3	432	9.1
Difference	____	___	101	14.9	-51.3	0.0	26.03	82.9	88.0	38.4	130	2.8

The reduction of flow rates due to flooding of the extraction column may be caused by two factors

1. Precipitation of solid matter on the packing of the column.
2. The build up of concentration of impurities in the solvent, thus changing its physical properties.

Run II:

The same sewage water sample was extracted using new redistilled solvent. High flow rates of both the water and solvent were possible at the start of the run, but due to flooding, flow rates had to be reduced as in Run I. The low flow rates of 2.0 l/hr. of water and 7.4 l/hr. of solvent were reached in a shorter time than in Run I.

In a period of $6\frac{1}{2}$ hours of operation, about 5.2 litres of solvent were recycled 11.3 times to extract 18.7 litres of sewage samples. Results were similar to those obtained in Run I, and are plotted in Figures 15 a, b and c. An average material balance is given in Table 19.

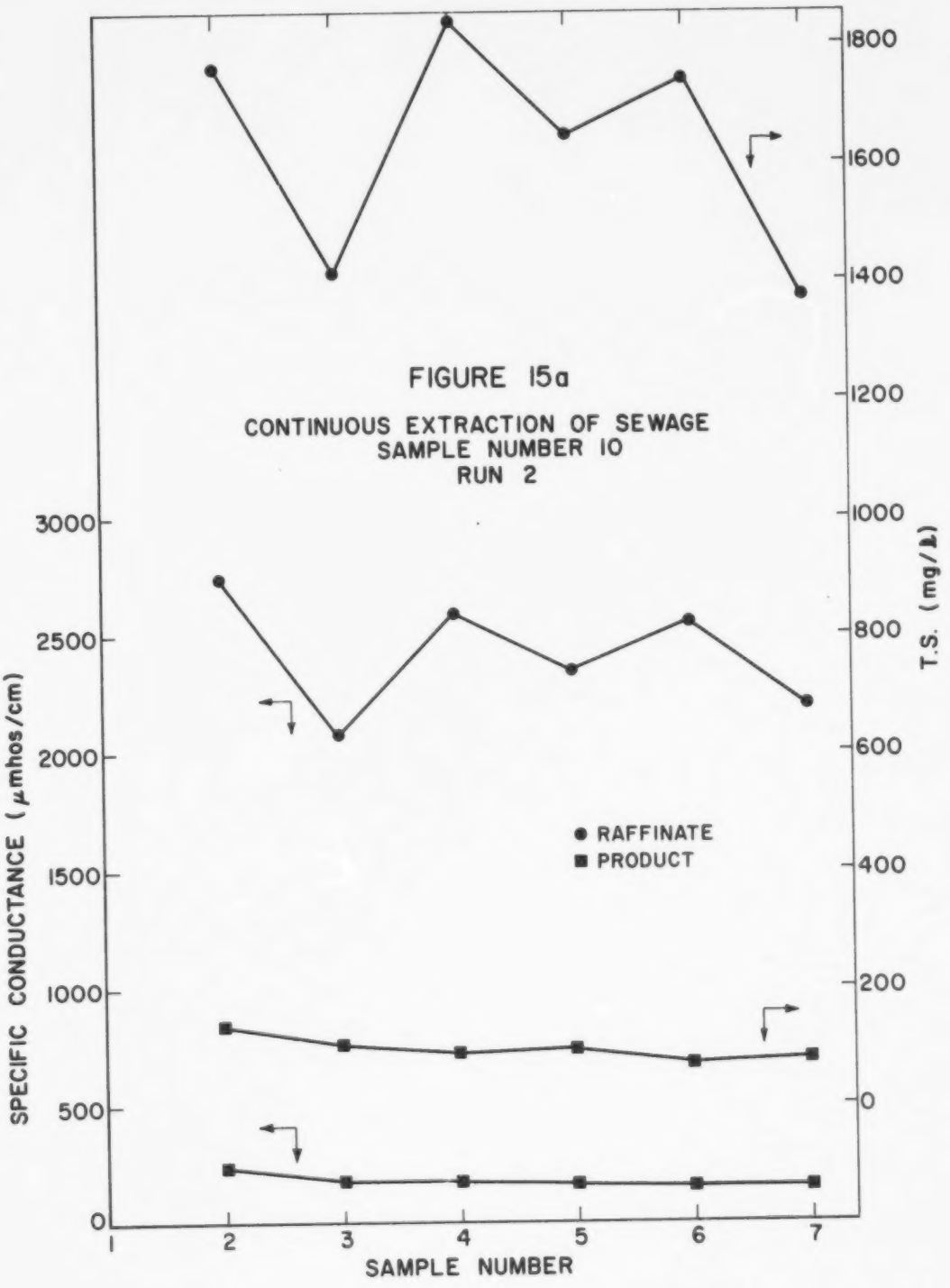


FIGURE 15a

CONTINUOUS EXTRACTION OF SEWAGE
SAMPLE NUMBER 10
RUN 2

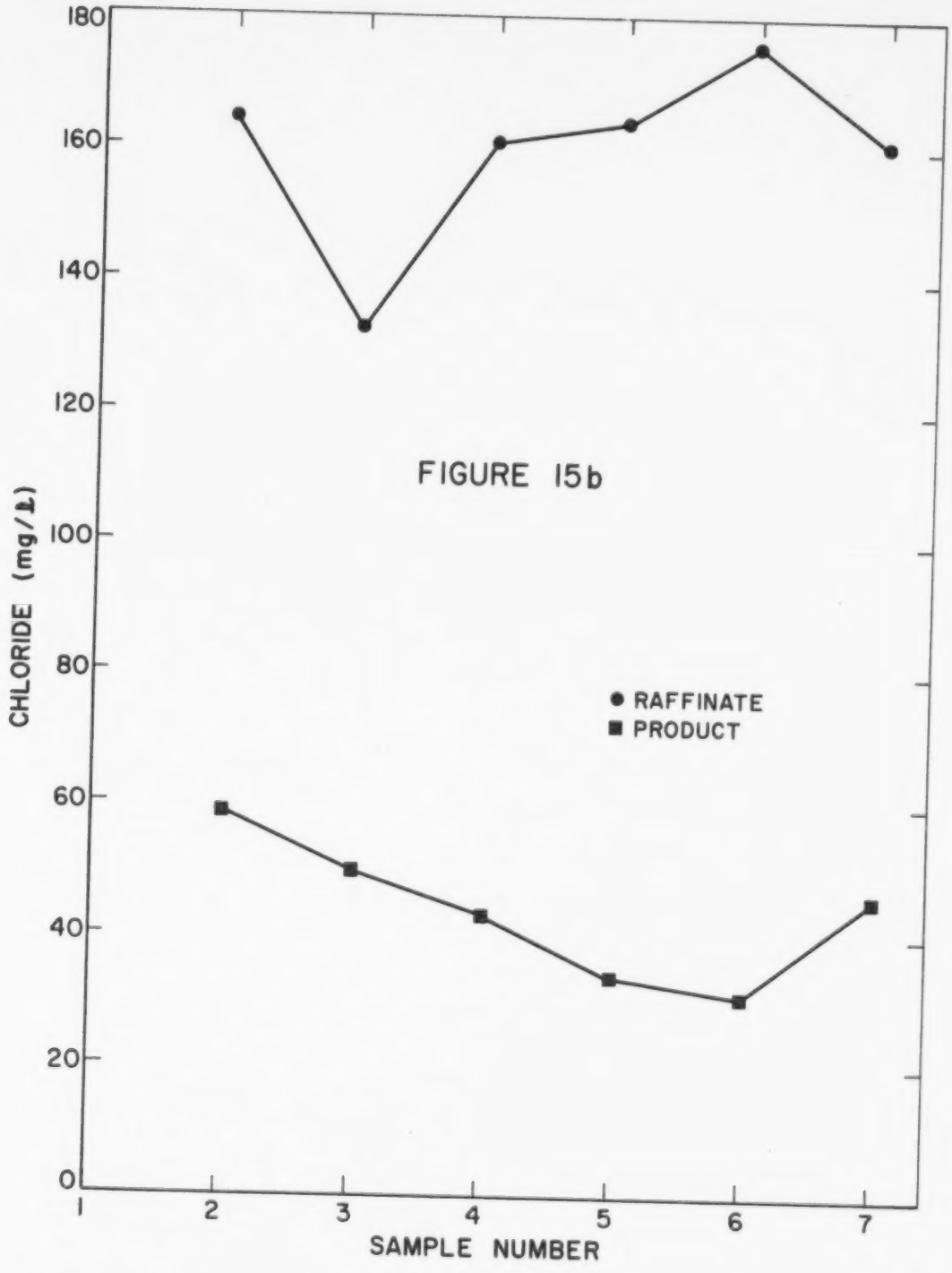

180
160
140
120
100
80
60
40
20
0
CHLORIDE (mg/L)
1
2
3
4
5
6
7
SAMPLE NUMBER
● RAFFINATE
■ PRODUCT

FIGURE 15b

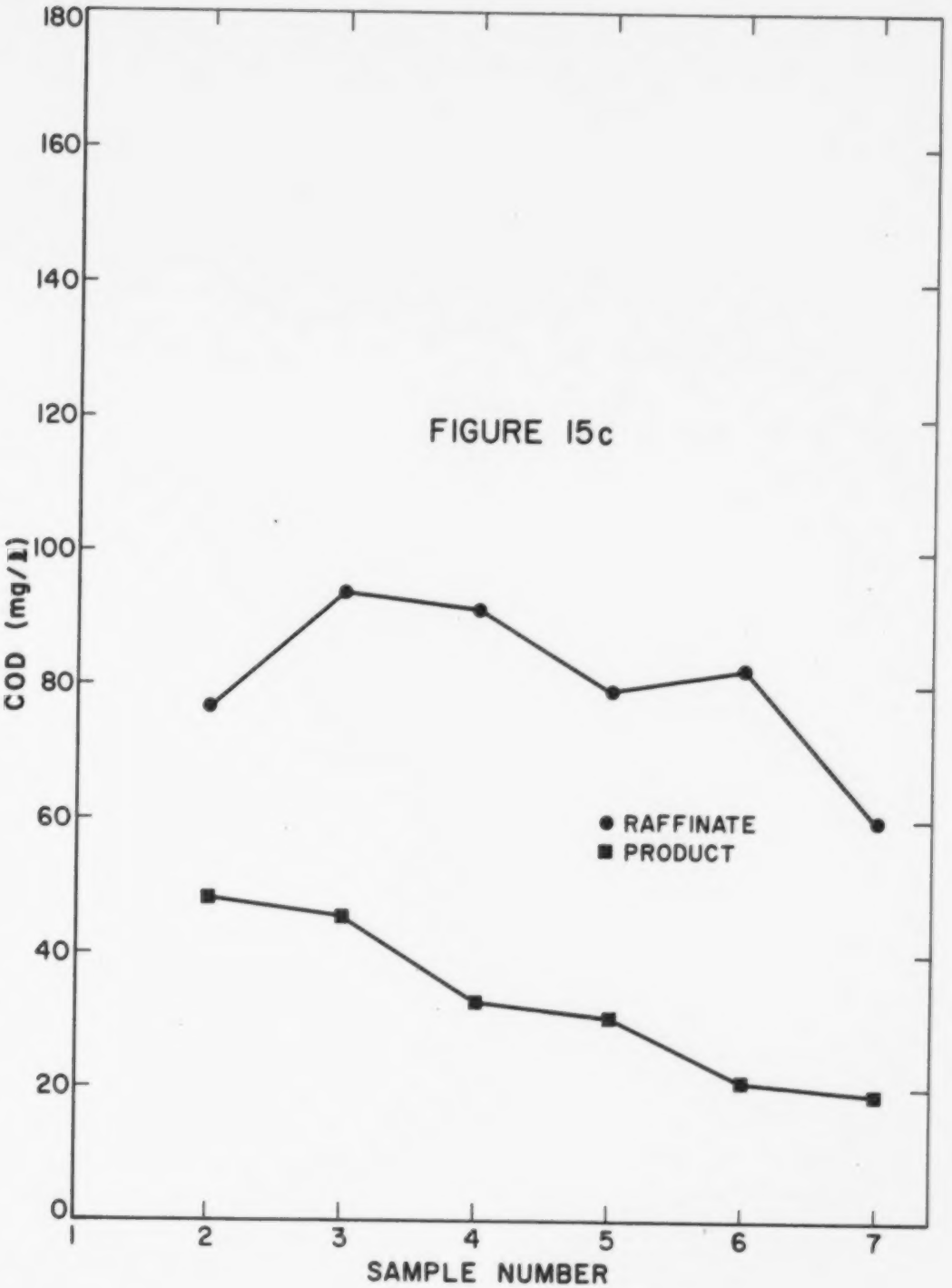

180
160
140
120
100
80
60
40
20
0
COD (mg/L)
1
2
3
4
5
6
7
SAMPLE NUMBER
RAFFINATE
PRODUCT

FIGURE 15c

Table 19

Average Material Balance and Per Cent Distributions of Contaminants

Run 11

	Weight		COD		Cl^-		ABS		PO_4^{---}		T. S.	
	gm	%	mg	%	mg	%	mg	%	mg	%	mg	%
Feed	8387	100	461.3	100	583	100	22.3	100	241.5	100	4990	100
Raffinate	2579	30.75	218.9	47.5	427.6	73.3	0.98	4.4	130.5	54	4201	84.2
Product	5808	69.25	150.1	32.5	189.9	26.7	8.94	40.0	1.9	0.8	558	11.2
Difference	———	———	93.3	20.0	-34.5	0.0	12.38	55.6	109.1	45.2	231	4.6

The results obtained by the extraction of filtered sewage secondary effluents indicate that the contamination of the solvent, and thus the change of its physical properties, especially viscosity, is the main factor affecting the flooding of the column. It was also found that solid matter precipitation on the packing of the columns contributes to its flooding.

It is believed that a great part of the solid matter precipitating on the packing is of a colloidal nature, as, for example, grease and other waxy materials. A pretreatment of the sewage water with a flocullant would remove both the phosphates and the waxy materials that contaminate the packing and the solvent. A preliminary study of this pretreatment is presented below.

Pretreatment of Secondary Effluents with a Coagulant prior to Solvent Extraction:

Preliminary tests were made on the coagulation of sewage effluents with ferric chloride and ferric sulfate. Batches of 150 ml. sewage water were made acidic, pH of 3, with a few drops of 5N sulfuric acid, then mixed with 0.1 and 0.05 ml of 1 M solutions of $FeCl_3$ and $Fe_2(SO_4)_3 \cdot nH_2O$. The samples were then made alkaline, pH of 9-10, to precipitate all the ferric ion, then centrifuged for 45 minutes at 3000 RPM. The treated samples were then analysed for COD.

An average reduction of 27% of the COD value was obtained with either $FeCl_3$ or $Fe_2(SO_4)_3$ solutions. The sewage sample used for this treatment was Sewage Sample No. 3 (See Appendix 1), after being filtered and stored at 4°C for 13 days. During storage the COD of the sample had dropped from 85.5 mg/l to 62.3 mg/l.

It is believed that flocculation of fresh sewage samples will result in higher percentage reduction of COD values than obtained with old samples used in this preliminary test.

Batch Extraction of Pretreated Sample:

Sewage Sample No. 8 was filtered, made acidic to a pH of 3 with 5N H_2SO_4, then mixed well with ferric sulfate solution. One batch was treated with 250 ppm $Fe_2(SO_4)_3$. and the other with 375 ppm. The two batches were then made alkaline, with NaOH, then centrifuged.

The treated samples were then extracted with double their weight of DIPA as described under batch extraction.

Table 20 shows the results of direct solvent extraction of sewage sample No. 8. It also includes the calculated per cent distribution of contaminants and their concentration ratios for the direct solvent extraction.

Table 21 shows the concentrations of COD, ABS, and Cl^- in the pretreated sample and the extraction streams for the batch pretreated with 250 ppm $Fe_2(SO_4)_3$ and the other batch pretreated with 375 ppm $Fe_2(SO_4)_3$.

The pre-treatment of sewage sample No. 8 resulted in no reduction of ABS or the Chloride ion, while a reduction of 46% to 50% of the COD value was obtained. When the pretreated samples were extracted with DIPA no significant change of COD concentrations in the raffinate and product was observed, while the COD concentration in the solvent phase was reduced to half the value obtained in direct DIPA extraction.

Table 20

Solvent Extraction of Sewage Effluent Sample No. 8

Feed -------- 800 ml Raffinate = 430 ml

DIPA --------1600 gm Product = 320 ml

Solvent = 1560 gm

	Chloride		COD		ABS		Sp. cond.	T.S.		T.S. calculated	
	mg/L	mg	mg/L	mg	mg/L	mg	μmhos/cm	mg/L	mg	mg/L	mg
Feed	57.3	46.8	120.7	98.3	4.9	3.92	778	438	350.4	438	350.4
Raffinate	89.8	38.6	169.0	72.7	0.16	0.069	1163	804	345.7	654.5	271.4
Product	28.0	8.9	58.5	18.7	0.24	0.077	186.6	100	32	104.9	33.6
Solvent	00.0	0.0	63.6	6.9*	3.1	4.83	---	---	---		45.4*
TOTAL		47.5		98.3		4.976					

*Calculated by difference.

	Per Cent Distribution					Ratio of Conc.	raffinate / product
	COD	Cl	ABS	T.S.(prac)	T.S.(Calc)	COD	2.89
Feed	100	100	100	100	100	Cl^-	3.20
Raffinate	74.0	81.3	1.4	91.5	77.4	T.S.	8.0
Product	19.0	18.7	1.6	8.5	9.6	Sp.cond.	6.25
Solvent	7.0	0.00	97.0	---	13.0		

Table 21

Ferric Sulfate Pretreatment Followed by DIPA Extraction

	DIPA Extraction			Pre-treated with 250 ppm $Fe_2(SO_4)_3$			Pre-treated with 375 ppm $Fe_2(SO_4)_3$		
	COD mg/l	ABS ppm	Cl^- mg/l	COD mg/l	ABS ppm	Cl^- mg/l	COD mg/l	ABS ppm	Cl^- mg/l
Sewage sample	123	4.9	58.5	123	4.9	58.5	114	4.9	58.5
Pre-treated sample	---	---	----	61.2	5.0	59.1	72	4.7	57.3
Raffinate	169	0.16	89.8	152	0.16	104.7	176	0.30	120
Product	58.5	0.24	28	56	0.24	30.6	56	0.36	35.4
Solvent	63.6	3.1	0.0	30	2.35	0.00	34	2.65	0.00

Continuous Extraction of Pre-treated Samples:

Several sewage secondary effluents were then coagulated and extracted in the continuous unit. The sample was treated with 500 mg/l of ferric sulfate at pH 3.5, then filtered. Regular flow conditions with no flooding were easily maintained for periods up to 12 hours during the extraction of coagulated samples.

The results of a typical run is given in the following table. The COD of the sewage effluent is reduced from 90.1 mg/l to 30.3 mg/l by coagulation. Solvent extraction further reduces the COD in the product below 12 mg/l. The recycle solvent, used to extract 36 liters of flocculated sewage water in 30 recycles has a COD concentration of 105 mg/1000 g and an ABS concentration of 22 mg/1000 g at the end of twelve hours.

Table 22

Continuous Extraction of Coagulated Sewage Sample with Diisopropylamine

	COD mg/l	ABS ppm	Cl^- mg/l	NO_3^- mg/l	PO_4^{---} mg/l	T.S. mg/l	V.S. mg/l	Conductivity μ mhos/cm
Sewage sample	90.1	2.52	71.0	43.8	26.00	744	198	-
Coagulated sample	30.3	2.60	-	-	0.00	720	190	-
Raffinate*	48.0	0.2-0.3	160-170	-	0.00	1890-2090	-	2790 - 3310
Product*	12.0	0.5-0.7	9-10	34-42	0.00	85-150	-	132 - 170

*Analysis is given as average or the range of samples collected during the last 7 hours of operation.

Continuous Extraction with Reflux:

Simple separatory funnel extractions had shown that the COD of the product produced was lower than that of the original water. Continuous countercurrent extraction of coagulated samples improved the quality of the product that could be obtained. Even so, the question remained whether the organics could be further reduced by extract reflux. This was not apparent since it is highly possible that there are organic constituents found in waste water which shown no selectivity in the solvent system being used, and the presence of these compounds would place a lower limit on the COD reduction that could be obtained by extraction.

Bench Scale Extraction System

It was decided that the packed column already in use would be used for the reflux system, and a Rotating Disc Contractor would be added to handle the raffinate because its open structure can easily accommodate any sludge that might precipitate in this section.

A diagram of the system is shown in Figure 16 and a photograph in Figure 17. The feed tank is an elevated 55 gallon drum from which the flocculated sewage or other water flows through a rotameter into the mixed-feed tank. Here it is mixed with the water from the bottom of the reflux tower and pumped through a rotameter to the top of the RDC column. The solvent water interface in this column is controlled by a U-tube on the raffinate line which empties into a raffinate accumulator.

FIGURE 16

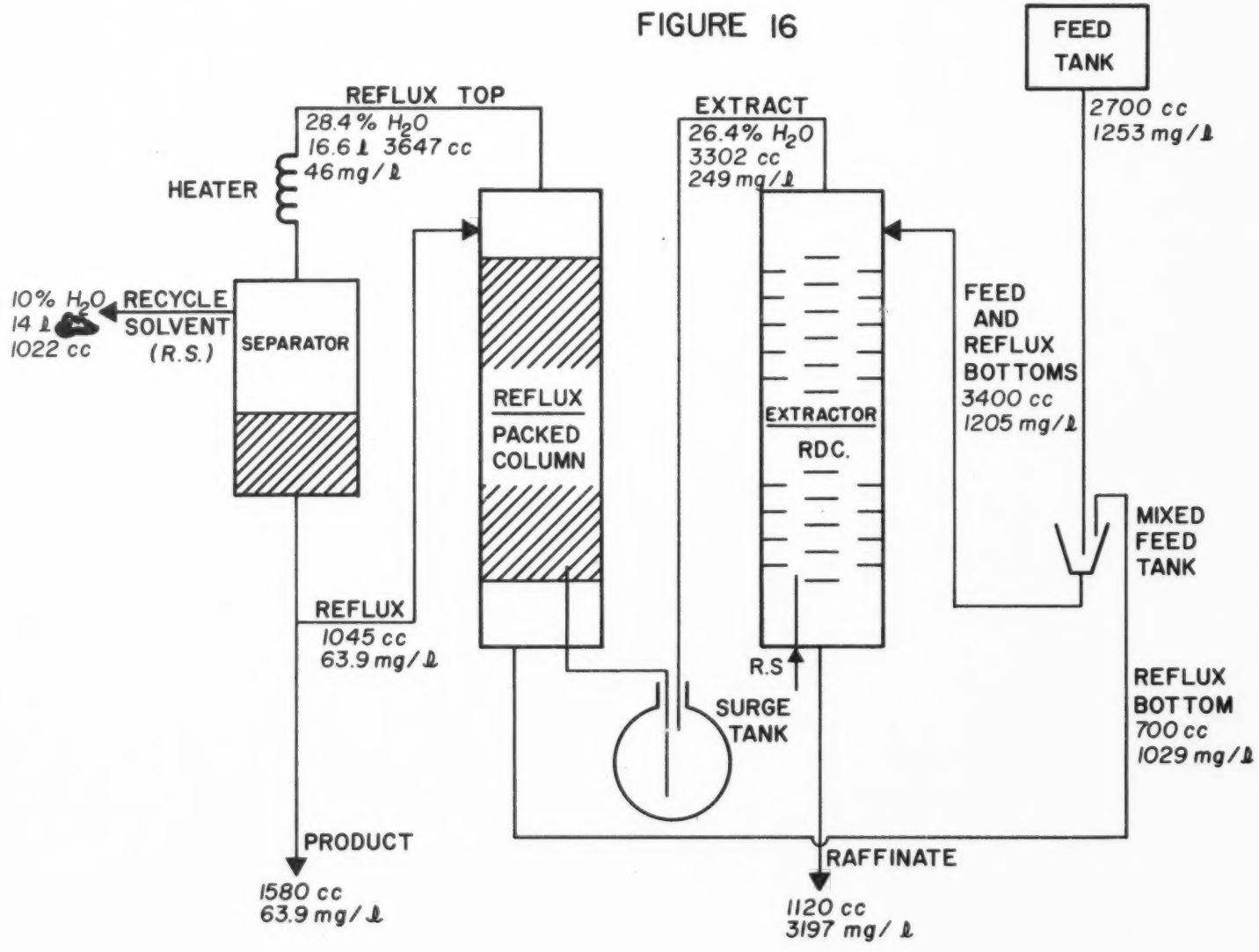
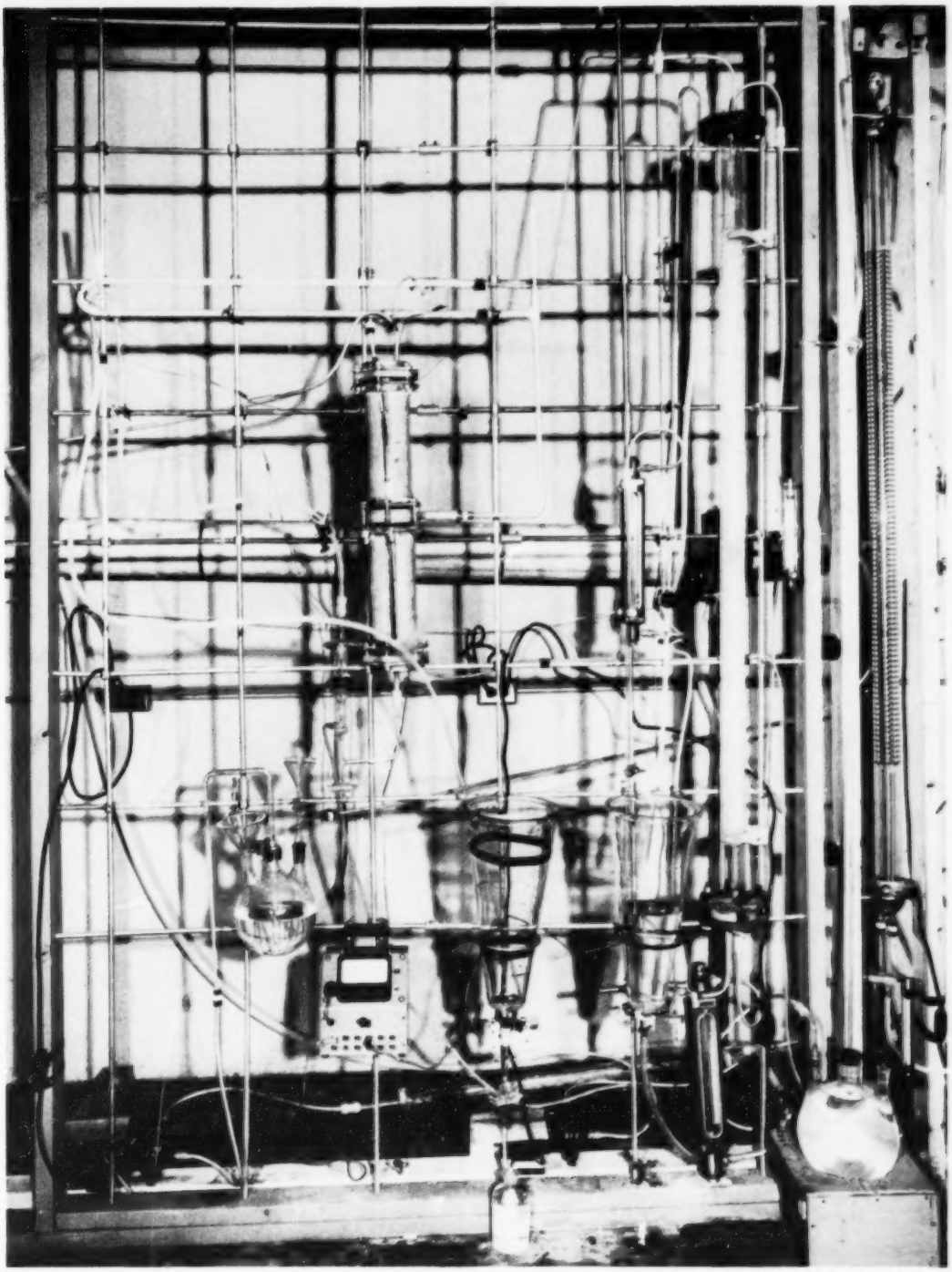

FEED TANK
2700 cc
1253 mg/ℓ
REFLUX TOP
28.4% H_2O
16.6 ℓ 3647 cc
46 mg/ℓ
EXTRACT
26.4% H_2O
3302 cc
249 mg/ℓ
HEATER
10% H_2O
14 ℓ
1022 cc
RECYCLE SOLVENT (R.S.)
SEPARATOR
REFLUX
PACKED COLUMN
EXTRACTOR
RDC.
FEED AND REFLUX BOTTOMS
3400 cc
1205 mg/ℓ
MIXED FEED TANK
REFLUX
1045 cc
63.9 mg/ℓ
R.S
SURGE TANK
REFLUX BOTTOM
700 cc
1029 mg/ℓ
PRODUCT
1580 cc
63.9 mg/ℓ
RAFFINATE
1120 cc
3197 mg/ℓ

Figure 17

Continuous Extraction System



Reproduced from
best available copy.

Solvent from the solvent surge tank is pumped through a rotameter into the RDC column and introduced just below the bottom mixing chamber. Extract from the top of this column overflows into the extract surge tank from which it is pumped into the bottom of the packed column just above the packing support. The interface in this column is also controlled by a U-tube through which water from the bottom of the column flows to the mixed-feed tank. Extract from the reflux column goes to a heater which consists of a glass tube wound with electrical heating tape. Here phase separation occurs, and the heterogeneous mixture is introduced at the center of a 3 liter separating vessel. The level in the separator is U-tube controlled with the water phase draining into a reflux accumulator from which reflux is pumped through a rotameter to the top of the packed column. Water product is withdrawn from the reflux accumulator.

In operating the unit, the recycled solvent, reflux and feed rate are kept constant. The mixed-feed rate is adjusted to maintain a constant level in the mixed-feed tank and constant levels are maintained in both columns and in the separator.

The RDC column is 2" in diameter and contains 96 mixing chambers spaced 1/2" apart. The disks are 13/16" in diameter and the stator ring openings are 1-13/32".

Both the packed and RDC columns seem to operate better with the solvent phase dispersed. Very small solvent droplets are formed in the packed column and only a low RPM is required to obtain good dispersion in the RDC column. Above 400 RPM, the solvent droplets

become so small as to be indistinguishable and of course column capacity is greatly reduced. In spite of the ease of dispersion, coalescing and settling is quite rapid and no tendency to form emulsions exists. With the water phase dispersed, a much higher RPM is required in the RDC column.

The temperature of the RDC column is controlled by cooling the recycled solvent. Since about 30 cal. are liberated per gram of water extracted, the solvent is introduced well below the 32° to 36°C temperature of the extract leaving the column. Only a little if any water is extracted in the reflux column which is externally wound with heating tape for temperature maintenance. Because of the extreme sensitivity of the water solubility to temperature, accurate control of temperature, especially in the reflux column, is very important. Variation in temperature in the column can result in an internal reflux rate markedly different from the apparent rate.

Results

It is difficult to obtain results on sewage which are accurate enough to give a good material balance because the low salt levels in some process streams result in fairly large analytical errors. For more accurate system evaluation, runs have been made on salt water. The results of such a run are shown in Figure 16.

The flow rates are given in cc's per hour on a solvent free basis except that the total flow of the recycled solvent and final extract are given in liters. The salt concentrations are expressed as mg/l of sodium chloride on a solvent free basis. Also the per

cent water in the extracts and solvent is noted. It may be seen that about 350 cc of water are extracted in the reflux column. Either the extract was not saturated in the RDC column or the temperature was lower in the packed column. Though basically due to poor control, this occurs frequently enough in the unit to make operation at low reflux rates difficult.

A graph showing the results of the run and the calculation of the number of theoretical stages in the packed column is shown in Figure 18. This is a weight ratio type diagram in which the solvent content divided by the water plus salt content is plotted on the ordinate and the fraction of salt divided by the fraction of salt plus water is plotted on the abscissa for both equilibrium phases. The solvent rich phase line would be nearly hroizontal except that the reflux tower was apparently non-isothermal, and a straight line was assumed to exist between the terminal concentrations. Because of large temperature changes in the RDC column for which the temperature profile is unknown, the graph was not extended to this section. About 2 1/2 theoretical stages are indicated for the packed column.

Table 23 shows results obtained on a particular sewage sample collected at the Bryan, Texas plant. The original sewage had a pH of 7.35. Twenty-three gms of ferric sulfate was added to 80 liters of this sewage and the pH was lowered to 3.4 by the addition of 90 ml of 5 N H_2SO_4. At this pH optimum flocculation occurs. After settling, the pH was brought to 8.5 with 110 ml of 2 N NaOH. The COD of this sewage sample was reduced from 57.3 to 35.5 mg/l.

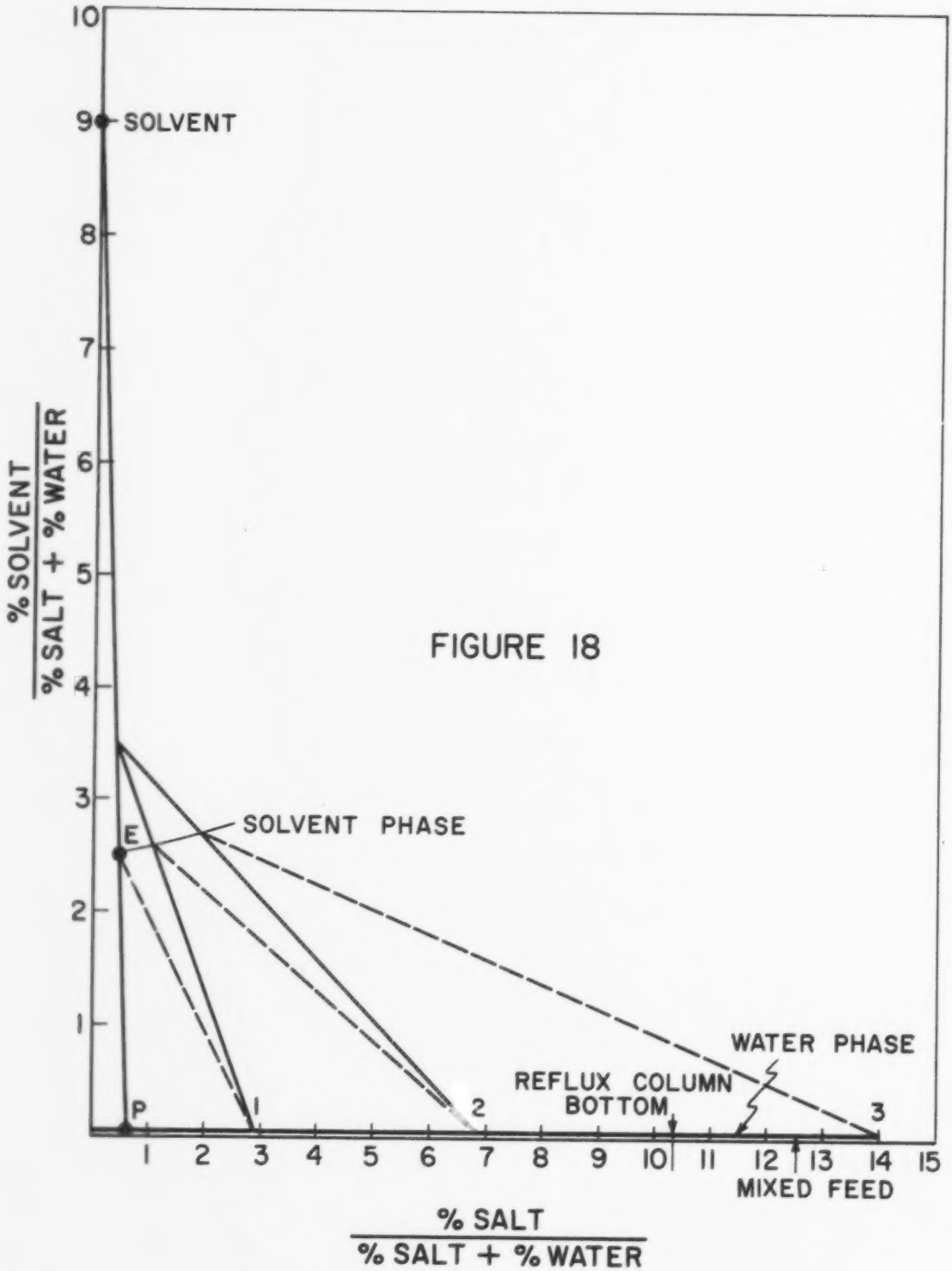

10
9
8
7
6
5
4
3
2
1
SOLVENT
% SOLVENT / % SALT + % WATER
SOLVENT PHASE
E
P
1
2
3
WATER PHASE
REFLUX COLUMN BOTTOM
MIXED FEED
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
% SALT / % SALT + % WATER

FIGURE 18

Table 23

EXTRACTION OF A SEWAGE USING REFLUX

Run No.		cl.mg/l.	COD mg/l.	Total Solids mg/l.
	Feed	49.6	35.5	850
1	Product	5	29.6	73
	Raffinate	106	42	1823
2	Product	2.6	6	67
	Raffinate	61.9	37.2	1400
3	Product	<2	<6	
	Raffinate	93	45.8	

The results listed in Table 23 are in order of increasing reflux, and the separation is seen to improve accordingly, although the high COD in run number one is probably abnormal. The lowest COD that has been obtained on any sewage sample without reflux is 12 mg/l and 20 mg/l is more typical.

Variations in extraction efficiency would be expected with different sewages. The data shown in Table 24 were obtained on four separate flocculated sewage samples to which additional NaCl had been added to allow accurate calculation of the number of theoretical stages. The results of these calculations are shown in Table 25. Notice how deceptive the external reflux ratio can be as a criterion for separation because of variation in the water content of both extract and solvent from the separator. The number of stages obtained are nearly constant agreeing well with the 2 1/2 stages obtained in Figure 18. From the four runs in Table 25, average values of the equilibrium constant for COD were calculated in the following manner:

It was assumed that the RDC column was equal to one theoretical stage; this will not cause great error because the change in concentration in the raffinate column is not great. This assumption was made necessary by incomplete COD analysis. From this assumption the concentration of COD in the extract entering the reflux column, $X_{E^{Pin}}$, is the raffinate concentration divided by K. It was also assumed that the number of stages for COD and salt were the same.

Table 24

EXTRACTION OF DIFFERENT SEWAGE SAMPLE WITH REFLUX

Run No.		cl.mg/l.	COD mg/l.	Total Solids mg/l.
	Feed	1240	29.4	3264
1	Product	41.2	18.5	175
	Raffinate	2770	36.3	9620
	Feed	933	27.0	2317
2	Product	6	1.5	34
	Raffinate	1386	39.3	2853
	Feed	1500	47.7	3318
3	Product	6.1	11.5	51
	Raffinate	2360	59	5252
	Feed	1540	25.5	3070
4	Product	20	8.5	100
	Raffinate	2200	32	4640

At constant extraction factor, the number of stages is given by

$$N = \frac{\log \left[\frac{X_{E\ out} - X_{reflux}/K}{X_{E\ in} - X_{reflux}/K} \right]}{\log \left[\frac{RK}{E} - 1 \right]}$$

Since N is known, this can be solved for K. The results are shown in Table 26.

Though the several assumptions may cast doubt on the quantitative nature of the results, it seems that sewage samples differ in selectivity and that some have good selectivities to quite low COD's. The extreme sensitivity of selectivity to water content exhibited by salt is not apparent for COD; although the lowest selectivity occurred at highest water content as would be expected, but there is no pattern beyond this. The reduction of COD by reflux is not as profound or predictable as the reduction of salt, yet the results obtained indicate that in these samples nearly all the organics can be removed, so that little if any material is present which exhibits no selectivity.

Table 25

THEORETICAL STAGES IN REFLUX COLUMN

Run No.	P	R/P	R/E	KR/E	N
1	41.2	.7	.30	1.59	1.8
3	6.1	.9	.30	3.60	2.3
4	20	1.33	.32	3.23	2.3
2	6	1.6	.44	3.78	2.3

Table 26

EQUILIBRIUM CONSTANTS FOR COD

Run No.	N	K	% H_2O In Extract
1	1.8	1.9	31
3	2.3	2.7	21
4	2.3	2.65	28
2	2.3	3.9	24.5

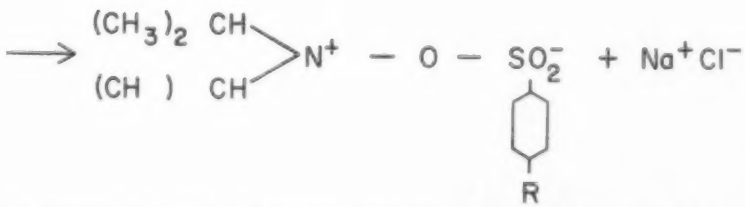
APPENDIX I

EXTRACTION OF ABS SOLUTIONS WITH DIPA

Diisopropyl amine was found to complete with methylene blue in the ABS analysis. Extraction of sewage effluents with DIPA removed over 90% of the ABS from both the raffinate and product, with the ABS being concentrated in the solvent phase. It was thought that ABS forms a complex with the amine.

Solubility of ABS - Amine Complex

A standard ABS solution, acidified with 1% HCl was reacted with the stoichimetric amount of pure DIPA, according to the following equation; where R in the ABS molecule stands for a dodecyl group.



Both the standard ABS solution and the ABS-DIPA complex solution, were contracted with chloroform and diethyl ether. The results

given in Table 1, indicate that ABS forms a complex with DIPA that is extractable with chloroform while ABS is not. Diethyl ether extracted both ABS and the ABS-DIPA complex.

Table 1

Extraction of ABS-DIPA Complex with Nonpolar Solvents

Sample	ppm ABS	
	Run 1	Run 2
(a) Standard ABS solution	10.9	11
(b) Standard ABS solution + DIPA	9.4	10
(c) Sample (a) extracted with chloroform	7.9	8.1
(d) Sample (b) extracted with chloroform	0.4	0.4
(e) Sample (a) extracted with diethyl ether	1.26	----
(f) Sample (b) extracted with diethyl ether	1.47	----

Extraction of Standard ABS Solutions with DIPA

a) Equal weights of standard ABS solution and DIPA were equilibrated for two hours at 32°C, then the raffinate separated. The extract was then heated to 50°C to exparate a product. The solvent was then distilled and the residue free of amine was diluted to a known volume. The analyzes for ABS in raffinate, product and solvent residue are given in Table 2.

Table 2

Extraction of Standard ABS Solutions with DIPA

Stream	Weight (gm)		ABS ppm		ABS ppm	
	Run I	Run II	Run I	Run II	Run I	Run II
Standard Solution	400	400	4.7	3.5	1.88	1.4
Raffinate	183	172	0.12	0.133	0.022	0.023
Product	138	150	0.21	0.200	0.029	0.030
Solvent	420	420	3.97	3.22	1.667	1.350
Error					-0.162	+0.003

In Run II, 96.4% of the ABS was extracted in the amine phase. The material balance gave an error of +0.003 mg of ABS.

b) Standard ABS solutions were equilibrated with one fourth its weight of DIPA, at 32°C. Higher concentration of ABS was used to determine the limiting value of the equilibrium constant K, which is calculated as the ratio of ABS concentration in the extract to that in the raffinate.

The results shown in Table 3 indicate that the extraction of ABS with DIPA involves an equilibrium, with a K value of 36 to 38 at 32°C.

Table 3

Equilibrium Concentration of ABS in Water-DIPA at 32°C

Ratio Solvent / Solution	ABS Concentration ppm			$K = \frac{\text{ABS extract}}{\text{ABS raffinate}}$
	Stand Solution	Raffinate	Extract	
1:4	4.8	0.5	18.07	36.14
1:4	20.8	2.05	78.7	38.40
1:1	17.60	0.24	9.02	37.60

Extraction of ABS from Sewage Secondary Effluents

To study the efficiency of ABS extraction from sewage secondary effluents the following two experiments were run:

a) Samples of different ABS concentrations were prepared by spiking a sewage sample that contained 0.96 mg/l of ABS. A volume of 300 ml. of each sample was extracted with 400 gm of pure DIPA at 32°C. The product was separated from the extract at 50°C. Results are given in Table 4.

Table 4

Extraction of ABS from Secondary Effluents

Feed		Raffinate		Extract		K_{ER} (1)	Product		Solvent		K_{SP} (2)
ppm	mg	ppm	mg	ppm	mg		ppm	mg	ppm	mg	
0.96	0.288	0.26	0.025	0.452	0.263	1.74	0.76	0.036	0.66	0.283	2.5
6.29	1.288	0.16	0.016	2.176	1.272	13.6	0.78	0.039	2.38	1.025	8.5
10.96	3.288	0.20	0.019	5.60	3.269	28	0.48	0.067	6.74	2.900	14.04
17.63	5.288	0.24	0.023	9.024	5.265	37.6	0.44	0.062	11.27	4.850	25.60

(1) $K_{ER} = \frac{\text{ABS concentration in Extract}}{\text{ABS concentration in Raffinate}}$ at 32°C

(2) $K_{SP} = \frac{\text{ABS concentration in Solvent}}{\text{ABS concentration in Product}}$ at 50°C

The apparent value of K increases with increasing ABS concentration, being higher at 32°C (extraction temperature) than at 50°C (separation temperature). This explains the slightly higher concentration of ABS in the product as compared to the raffinate.

b) A sewage sample containing 4.47 ppm ABS was extracted with different DIPA to feed ratios. The per cent distribution of ABS in the extraction streams is given in Table 5.

Table 5

Distribution of ABS in Extraction Streams

Feed Volume DIPA Weight	300 ml 400 gm		200 ml 400 gm		150 ml 400 gm	
	ABS		ABS		ABS	
	mg	%	mg	%	mg	%
Feed	1.341	----	0.894	----	0.671	----
Raffinate	0.08	6.2	0.048	5.3	0.017	2.5
Product	0.004	3.4	0.047	5.2	0.051	7.7
Solvent	1.163	90.4	0.813	89.5	0.600	89.8
Total	1.287	100.	0.908	100.	0.668	100.

The solvent phase extracted 90% of the total ABS. The remainder 10% distributed between the raffinate and product depending on the DIPA: Feed ratio which determines the weight ratic of raffinate to product.

APPENDIX II

ANALYSIS OF SECONDARY EFFLUENT SAMPLES

Sample I

Secondary effluent from College Station Sewage Plant. Date - October 17, 1962.

The sample was filtered through Whatman No. 3 filter paper using Celite as a filter aid.

Analysis

Chloride	=	50.3	mg/l
ABS	=	3.42	ppm
T.S.	=	529	mg/l
V.S.	=	385.5	mg/l
COD	=	264	mg/l
pH	=	7.9	

The change of COD values for the filtered sample stored at room temperature is given below:

COD values - mg/l

original	1 day	2 days	6 days	9 days
264	76.4	60.6	29.2	27.5

These values are plotted in Figure 1.

N.B. The large drop of COD from 264 to 76.4 mg/l during the first day of storage is due to bacterial action and to settling of particles that passed through the Whatman No. 3 filter paper.

Sample 2

Secondary Effluent from Texas A&M University Sewage Plant. Date - November 12, 1962.

The sample was filtered through Whatman No. 5 filter paper and pasteurized, then stored at 4°C in the cold room.

Analysis

Chloride	=	61.36	mg/l
COD	=	84.6	mg/l
ABS	=	0.96	ppm
T.S.	=	583.0	mg/l
V.S.	=	134.0	mg/l
pH	=	7.72	

COD values (mg/l)

	original	2 days	4 days	7 days	14 days
Filtered sample	84.6	70.3	58.9	30.7	24.4
Pasteurized sample	84.6	87.5	84.8	87.6	78.8

These values are plotted in Figure 32.

Sample 3

Secondary Effluent from Bryan Sewage Plant. Date - November 28, 1962.

The sample was filtered (Whatman No. 5) and pasteurized, then stored at 4°C in the cold room.

Analysis

Chloride	=	45.8	mg/l
COD	=	85.5	mg/l
ABS	=	4.47	ppm
T.S.	=	417	mg/l
V.S.	=	144.5	mg/l
sp. conductance	=	632.4	mhos/cm

COD values (mg/l)

	original	2 days	5 days	8 days	10 days	13 days
Filtered sample	85.5	77.3	67.2	39.2	39.6	--
Pasteurized sample	85.5	87.4	77.2	76	77.0	61.7

These values are plotted in Figure 3.

Sample 4

Secondary effluent from Bryan Sewage Plant. Date - December 17, 1962.

The sample was filtered (Whatman No. 5) and pasteurized, then stored at 4°C in the cold room.

Analysis

Chloride	=	56.15	mg/l
COD	=	110.5	mg/l
ABS	=	6.0	ppm
T.S.	=	486.0	mg/l
V.S.	=	162.5	mg/l
sp. conductance	=	780	µmhos/cm

$$\text{Ratio } \frac{\text{dissolved residue}}{\text{sp. conductance}} = 0.624$$

$$\text{Ratio } \frac{\text{fixed residue}}{\text{sp. conductance}} = 0.415$$

COD values (mg/l)

	original	2 days	4 days
Filtered sample	110.5	101.9	106.9
Pasteurized sample	110.5	76.5	79.4

These values are not plotted, since the fresh sample was used only once.

Sample 5

Secondary effluent from Bryan Sewage Plant. Date - January 7, 1963.

The sample was filtered (Whatman No. 5) and pasteurized, then stored at 4°C in the cold room.

Analysis

Chloride	=	60.4	mg/l
COD	=	87.7	mg/l
ABS	=	4.4	ppm
T.S.	=	462	mg/l
V. S.	=	140	mg/l
Specific conductance	=	742.7	μmhos/cm

$$\text{Ratio } \frac{\text{dissolved residue}}{\text{sp. conductance}} = 0.622$$

$$\text{Ratio } \frac{\text{fixed residue}}{\text{sp. conductance}} = 0.433$$

COD values (mg/l)

	original	2 days	4 days	7 days
Filtered sample	84.2	87.7	87.7	78.2
Pasteurized sample	84.2	66.1	56.5	59.5

Sample 6

Secondary effluent from Bryan Sewage Plant. Date - January 22, 1963.

The sample was filtered (Whatman No. 5) and pasteurized, then stored at 4°C in the cold room.

Analysis

Chloride	=	67.3	mg/l
COD	=	113.3	mg/l
ABS	=	6.72	ppm
T.S.	=	560	mg/l
V.S.	=	200	mg/l
sp. conductance	=	813	μmhos/cm

$$\text{Ratio } \frac{\text{dissolved residue}}{\text{sp. conductance}} = 0.688$$

$$\text{Ratio } \frac{\text{fixed residue}}{\text{sp. conductance}} = 0.442$$

COD values (mg/l)

	original	6 days	8 days
Filtered sample	113.3	108.4	100.7
Pasteurized sample	113.3	71.7	60.3

Sample 7

Secondary effluent from Bryan Sewage Plant. Date - February 12, 1963.

Analysis

Chloride	=	53.7	mg/l
COD	=	87.3	mg/l
ABS	=	4.7	ppm
T.S.	=	411	mg/l
V.S.	=	286	
sp. conductance	=	709	μmhos/cm

This sample was collected Tuesday morning following a rainfall during Sunday and Monday.

Sample 8

Secondary effluent from Bryan Sewage Plant. Date - February 26, 1963.

The sample was filtered (Whatman No. 5) and pasteurized, then stored at 4°C in the cold room.

Analysis

Chloride	=	57.3	mg/l
COD	=	120.7	mg/l
ABS	=	4.7	ppm
T.S.	=	438	mg/l
V.S.	=	128	mg/l
sp. conductance	=	778	μmhos/cm

$$\text{Ratio } \frac{\text{dissolved residue}}{\text{sp. conductance}} = 0.563$$

$$\text{Ratio } \frac{\text{fixed residue}}{\text{sp. conductance}} = 0.400$$

COD values (mg/l)

	original	2 days	6 days	12 days	14 days
Filtered sample	120.7	101.2	67.7	42.4	---
Pasteurized sample	120.7	122.8	118.7	123.2	114.0

Sample 9

Secondary effluent from Bryan Sewage Plant. Date - April 8, 1963.

The sample was filtered (Whatman No. 5) then used as feed to the continuous unit.

Analysis

Chloride	=	60.2	mg/l
COD	=	88.3	mg/l
ABS	=	3.7	ppm
T.S.	=	434	mg/l
V.S.	=	134	mg/l
sp. conductance	=	730	μmhos/cm
NO_3^-	=	9.5	ppm
PO_4^{---}	=	18.8	ppm

$$\text{Ratio } \frac{\text{dissolved residue}}{\text{sp. conductance}} = 0.600$$

$$\text{Ratio } \frac{\text{fixed residue}}{\text{sp. conductance}} = 0.411$$

Sample 10

Secondary effluent from Bryan Sewage Plant. Date - April 18, 1963.

The sample was filtered (Whatman No. 5) then used as feed to the continuous unit.

Analysis

Chloride	=	69.5	mg/l
COD	=	85	mg/l
ABS	=	3.9	ppm
T.S.	=	595	mg/l
V.S.	=	200	mg/l
sp. conductance	=	900	μmhos/cm
NO_3^-	=	43	ppm
PO_4^{---}	=	28.8	ppm

N.B.: This sample was filtered through a continuous filter under pressure. The filter paper broke several times, and the filtration was not complete. The COD was 180 mg/l, but after one day settlement the clear sewage had a COD of 85 mg/l.

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